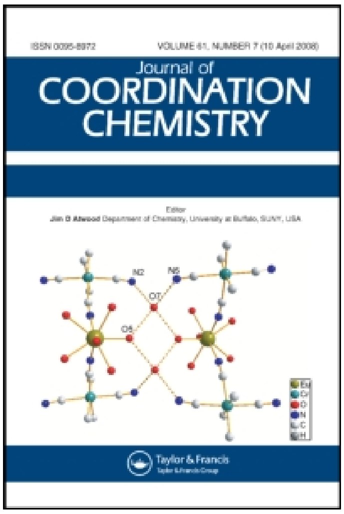

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KINETIC STUDIES OF LEWIS BASE ADDITION TO CpFe(CO)(η^3-$CH_2C_6H_4$-p-X); X = OMe, Me, H,F, Cl, Br[†]

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Kinetic studies illuminate details of the reaction of photoproduced CpFe(CO)(η^3-$CH_2C_6H_5$) with two electron Lewis bases. Rate constants of 151(10)$M^{-1}s^{-1}$ for CO back reaction and between 440 and 3200 $M^{-1}s^{-1}$ for reaction with various phosphine nucleophiles were recorded. Linear free energy analysis quantifies the stereoelectronic effect of the nucleophile. Variation of the para-substituent on the benzyl group demonstrates that an electron rich benzyl group impedes reaction. The effect of ancillary ligands was seen by substitution of C_5Me_5 for C_5H_5. The large, electron rich C_5Me_5 speeds up CO substitution but slows down PPh_3 substitution. Mechanistic clues were obtained from Eyring plots for reaction of CpFe(CO)(η^3-$CH_2C_6H_5$) with 4 different phosphines. Examination of the measured enthalpy and entropy barriers suggests a stepwise reaction mechanism.

KEYWORDS: flash photolysis, kinetics, iron benzyl

INTRODUCTION

The utilization of flash photolysis to analyze reactions of metal carbonyl transients has added greatly to our mechanistic understanding of ligand substitution reactions. Among the discoveries made with this technique is that 16-electron transients formed following carbon monoxide loss have only a fleeting existence and do not react directly with incoming nucleophiles. These true 16-electron transients instead have a lifetime typically measured in picoseconds.[1] A very common transformation for these high energy fragments is reaction with a solvent molecule from the solvent cage. This process occurs within a few picoseconds of ligand loss. Studies on $Cr(CO)_6$ serve as a paradigm for this mechanism.[2] Although the solvent is very weakly bound, it nonetheless forms a covalent interaction with the metal center and occupies the vacant coordination site. Spectral and kinetic studies on a wide variety of interacting species and various metal complexes have shown that this process is widespread.[2,3,4]

A process which can occur instead of, or after, solvation is rearrangement giving intramolecular stabilization. Two examples of this are $Mn_2(CO)_8(\mu$-η^1:η^2-CO) and

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[†] Dedicated to Prof. Theodore L. Brown on the occasion of his 65th Birthday
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$CpFe(\mu\text{-}CO)_3FeCp$. $Mn_2(CO)_8(\mu\text{-}\eta^1{:}\eta^2\text{-}CO)$ is stabilized after CO dissociation from $Mn_2(CO)_{10}$ by π donation from a CO on the adjacent manganese center to bring the electron count at each metal to 18.[5] Recent work establishes how it is formed. Zhang and Harris identified the $Mn_2(CO)_9$ photoproduct present 2-3 ps after photolysis of $Mn_2(CO)_{10}$.[6] Zhang, Zhang and Brown showed that this intermediate can form a solvento species at 93 K in 3-methylpentane prior to conversion to the relatively more stable linear semibridging intermediate.[7] $CpFe(\mu\text{-}CO)_3FeCp$ is formed by CO dissociation from $[CpFe(CO)_2]_2$ followed by rearrangement.[8] Each of these dimers is unstable although the structure of the diiron compound was verified by a molecular structure for the Cp^* derivative.[9]

We have become interested in the reactivity of intermediates stabilized by electron donation from a bound hydrocarbon. In particular we are concentrating on the reaction dynamics in cases where the interaction is insufficient to provide an isolable complex. An example of this is the study of $CpFe(CO)_2(\eta^1\text{-}C_5H_5)$ reported by Wrighton and co-workers.[10] Photoinduced CO loss generates the formally 18-electron intermediate, $CpFe(CO)(\eta^3\text{-}C_5H_5)$, which ($k = 1.37 \times 10^{-4}s^{-1}$ at 166 K) extrudes the remaining carbon monoxide ligand forming ferrocene.

Our efforts are aimed at analyzing the reactivity of η^3-benzyl systems formed by photoinduced CO loss. These systems are structurally similar to η^3-allyl compounds.[11] The primary difference between the two is that the η^3-benzyl interaction is much less stable than the η^3-allyl interaction. This can be attributed to the resonance energy of the phenyl ring which must be overcome to obtain an η^3-interaction. A structural study of $CpMo(CO)_2(\eta^3\text{-}CH_2C_6H_5)$ showed a longer Mo-C bond for the two bound phenyl carbons[11b] than for the corresponding η^3-allyl system.

Previous workers have shown that $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ readily photodissociates carbon monoxide forming $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$

$$CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5) \xrightarrow{h\nu} CpFe(CO)(\eta^3\text{-}CH_2C_6H_5) \qquad (1)$$

The photoproduct has been studied by low temperature NMR[12] and infrared and electronic spectroscopy.[13] While the compound cannot be isolated it can be studied in solution at low temperatures or at room temperature for short periods of time in the absence of Lewis bases.

The intermediate is rapidly trapped by Lewis bases forming the η^1-benzyl product (eq 2).

$$CpFe(CO)(\eta^3\text{-}CH_2C_6H_5) + L \rightarrow CpFe(CO)L(\eta^1\text{-}CH_2C_6H_5) \qquad (2)$$

We have performed extensive kinetic studies on the reactivity of $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ toward Lewis base nucleophiles following photoinduced CO loss.[14] This paper reports the steric and electronic effect of phosphine nucleophiles, the effect of benzyl and cyclopentadienyl substituents on the rate, and evidence supporting a stepwise mechanism of ligand addition to $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$.

EXPERIMENTAL

Materials

Materials for flash photolysis were prepared and purified using literature methods.[15] Solvents for flash photolysis were purified as described previously.[16] Phosphines were stored under nitrogen. Phosphites were distilled prior to use and stored under nitrogen.

Spectroscopic Measurements

Infrared spectra were recorded on a Perkin-Elmer Lambda 4C spectrometer. A Sunpak 321 S camera flash with a color temperature of 5500 K was used to flash solutions in IR cells. The apparatus, experimental procedure, and data analysis for routine xenon lamp flash photolysis experiments have been described elsewhere.[10a] Variable temperature flash photolyses were conducted using a 28 mm (diameter) by 85 mm (length) cell with a 1 mm water jacket. The cooling solution was circulated through the jacket of the photolysis cell by a Fisher Scientific Model 900 temperature bath. Temperatures were maintained to within ±0.05°C. Temperature readings were corrected over the range 10–60°C with a calibrated thermometer by measuring actual cell temperatures for comparison to the water bath temperatures before variable temperature experiments.

Infrared Studies

A hexane solution of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ with PPh_3 in 10-fold excess was flash photolyzed with a Sunpak 321 S camera flash several times. The progress of the photochemical reaction was followed by IR. After one flash the difference spectrum shows the two carbonyl peaks of the starting material disappearing and a band at 1917 cm^{-1} due to $CpFe(CO)(PPh_3)(\eta^1\text{-}CH_2C_6H_5)$ growing in.[13] Repeated flashes showed the reaction proceeding to completion.

RESULTS AND DISCUSSION

Establishment of the Rate Law

Previous work has shown that flash photolysis of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in alkane solvent produces $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ as the CO loss product.[13] In hexane at 21°C under 1 atm of carbon monoxide a completely formed transient is apparent at the end of the lamp pulse. The transient decays exponentially back to the original baseline in about 3 s. The transient absorption spectrum, assigned to $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$, displays a maximum absorbance at 460±5 nm (Figure 1) in agreement with the 196 K spectrum of $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ in methylcyclohexane.[13] In contrast $Cr(CO)_5$(alkane), for example, disappears on the microsecond time scale under a CO atmosphere.[2] Repeating the experiment on $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in perfluorohexane under CO gives an observed rate constant only 5 times faster than that observed in hexane.[17] This experiment has previously been used to test for an intermediate with a solvent in the coordination sphere, because diffusion-controlled reaction rates are typically observed for solvated intermediates in perfluoroalkane solvents. The long lifetime and the slight dependency on solvent rules out the possibility of a solvated intermediate.

Variation of the carbon monoxide concentration results in a linear change in the observed rate (Figure 3). This is consistent with a mixed-second order rate law with L = CO (eq 3).

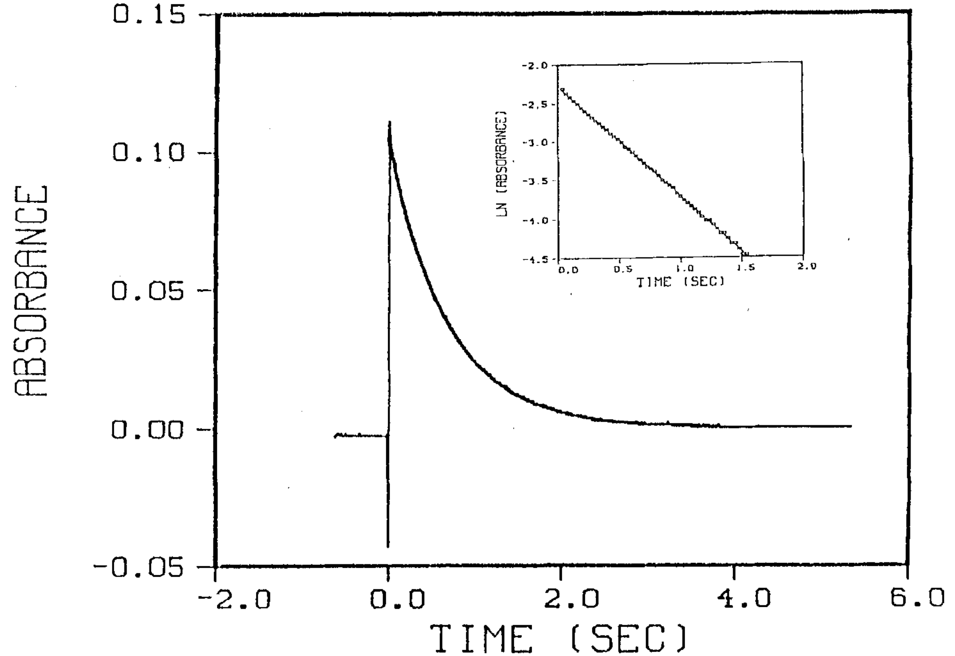


Figure 1 Change in absorbance vs time at 460 nm on flash photolysis of a CO saturated hexane solution of Cp-Fe(CO)$_2$(η^1-CH$_2$C$_6$H$_5$) The line through the decay curve represents the nonlinear first-order least-squares fit of the data for the disappearance of the transient. Insert: linear least-squares first-order fit of the data to 3.1 half-lines; R = -0.9998.

$$R = k[CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)][L] \qquad (3)$$

The bimolecular rate constant for reaction with CO is 151(10) $M^{-1}s^{-1}$.[18]

Flash photolysis experiments are nearly photochromic except that after 5 or more flashes a second minor transient is apparent which rapidly decays over a few milliseconds. This is presumed to be due to the formation of *exo*-(η^4-C$_5$H$_5$CH$_2$C$_6$H$_5$)Fe(CO)$_3$. It was previously observed in alkane solvent under CO following Fe-CH$_2$C$_6$H$_5$ bond homolysis.[13] The quantum yield for this chemical event is much smaller than for Fe-CO bond cleavage, hence *exo*-(η^4-C$_5$H$_5$CH$_2$C$_6$H$_5$)Fe(CO)$_3$ should build up slowly with repeated flashing. It is expected to produce a CO deficient transient upon photolysis which will rapidly regain CO, as observed. The presence of this transient did not affect the reaction kinetics of CpFe(CO)(η^3-CH$_2$C$_6$H$_5$) and will not be considered further.

Flash photolysis experiments with a phosphine present in excess also produce an exponential decay, but to a new baseline of higher absorbance. The solutions change from yellow to orange upon a single flash, consistent with the formation of a new species which absorbs more intensely at 460 nm. Previous work has shown that CpFe(CO)(η^3-CH$_2$C$_6$H$_5$) traps phosphine nucleophiles producing the monosubstituted product, CpFe(CO)(PR$_3$)(η^1-CH$_2$C$_6$H$_5$) (eq 2 with L = PPh$_3$).[12,13] The infrared spectrum of a solution of CpFe(CO)$_2$(η^1-CH$_2$C$_6$H$_5$) and PPh$_3$ in hexane in an IR cell showed an intense band at 1917 cm^{-1} due to CpFe(CO)(PPh$_3$)(η^1-

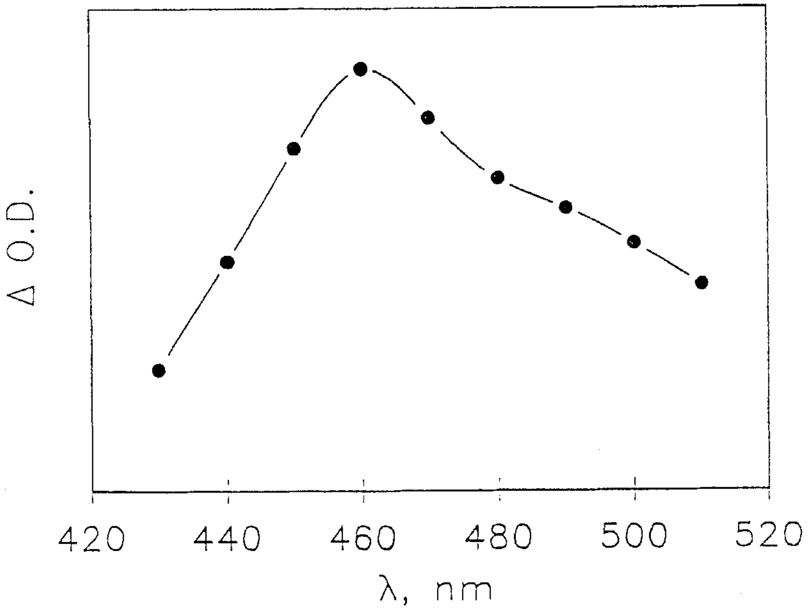


Figure 2 Electronic spectrum of the transient observed following flash photolysis of CpFe(CO)$_2$(η^1-CH$_2$C$_6$H$_5$) in hexane. Data were obtained by measuring the optical density immediately after the flash at several wavelengths. A λ_{max} of 460 ± 5 nm was measured.

CH$_2$C$_6$H$_5$) after a single burst from a camera flash, confirming that this was the reaction monitored.

The linear variation of the observed rate constant against PPh$_3$ concentration (Figure 3) proves that reaction of the transient with phosphines is first order in both the transient and phosphine. A bimolecular rate constant of 1.34(5) × 10^3 M^{-1}s^{-1} was obtained for reaction with PPh$_3$.

Effect of the Nucleophile on the Rate

Bimolecular rate constants of the trapping reaction for 16 phosphines have been measured (Table 1). Rates between 440 M^{-1}s^{-1} and 3200 M^{-1}s^{-1} have been observed. Thus, all phosphines react more rapidly with CpFe(CO)(η^3-CH$_2$C$_6$H$_5$) than does CO. The quantitative effect of the phosphine was investigated by considering both the electronic and steric effect of the phosphine on the rate constant. By assuming that the energy barrier is composed of electronic (log k_{el}) and steric (log k_{st}) components it is possible to apply linear free energy relationships to extract information about the reaction (eq 4)[19].

$$\log k = \log k_{el} + \log k_{st} + c \tag{4}$$

It has been known for a number of years that reactions containing an incoming phosphorus (III) nucleophile show an electronic effect based only on the σ-donor ability of the phosphine, even for phosphites which can act as strong π-acids in ground state complexes.[20] The lack of π-effect in the transition state is presumably

Table 1 Bimolecular rate constants for the addition of Lewis bases to $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ in hexane at 21 ± 1 °C. χ_d is the phosphine electronic parameter and θ is the phosphine steric parameter.

No.	PR_3	k, $M^{-1}s^{-1}$	χ_d	θ
1	PMe_3	3.0×10^3	8.55	118°
2	PMe_2Ph	3.2×10^3	10.60	122°
3	PPh_2H	1.8×10^3	17.35	125°
4	$P(OMe)_3$	1.2×10^3	16.70	128°[a]
5	$P(OPh)_3$	4.4×10^2	22.05	128°[b]
6	$P(OEt)_3$	1.1×10^3	15.51	134°[a]
7	$PMePh_2$	2.3×10^3	12.10	136°
8	PEt_3	1.7×10^3	6.30	137°[a]
9	$P(C_6H_4\text{-p-Cl})_3$	1.1×10^3	16.80	145°
10	$P(C_6H_4\text{-p-F})_3$	7.7×10^2	15.70	145°
11	PPh_3	1.3×10^3	13.25	145°
12	$P(C_6H_4\text{-p-Me})_3$	1.3×10^3	11.50	145°
13	$P(C_6H_4\text{-p-OMe})_3$	1.6×10^3	10.50	145°
14	PPh_2Cy	8.4×10^2	9.40	153°
15	PPr^i_3	6.4×10^2	3.45	160°
16	PCy_3	4.4×10^2	1.40	170°

[a] Cone angles represent updated values.[c]
[b] Uncorrected cone angle. The actual value should be larger.[c]
[c] Stahl, L.; Ernst, R. D. *J. Am. Chem. Soc. 109*, 5673(**1987**).

due to long metal-phosphorus bond lengths in the transition state. Since π-interactions decrease more rapidly with distance than do σ-interactions, the π-interaction is negligible in the transition state.[21] Experimental evidence for the sensitivity of the phosphite-metal π-interaction as a function of distance was gleaned from heats of reaction studies for eq. 5.[22] The data agree with a σ-interaction alone despite the fact that $P(OPh)_3$ has been observed to be a strong π-acid in other compounds.[23]

$$Mo(CO)_3(\eta^6\text{-}C_7H_8) + 3P(OPh)_3 \rightarrow Mo(CO)_3[P(OPh)_3]_3 + C_7H_8 \qquad (5)$$

The explanation proposed was that steric congestion, which probably increases the metal-phosphorus distance, leads to purely σ-donor behaviour from the ligands.

The pK_a of HPR_3^+ has often been used to measure σ-donicities, but recent work has shown this factor to contain a dependence on steric bulk. Giering *et al.* have introduced the use of a new parameter, χ_d, as a measure of the σ-donicity for phosphines, including those which contain a π bonding component.[2] It is derived from the ν value originally put forth by Tolman, but subtracts out any π-bonding electronic effects.

The electronic effect of the phosphine was obtained by solving for log k *vs.* $a\chi_d + b$ for the 5 isosteric triarylphosphines studied. The linear regression produces $a = -0.035$ and $b = 3.6$ with a correlation coefficient of 0.81. The negative sign associated with a is consistent with the increased σ donicity accelerating the rate constant as expected. Figure 4 shows the plot of log k *vs.*χ_d for all phosphines studied.[24] The line is the calculated regression line for the 5 isosteric phosphines.

The experimental value of log k_{st} + c for each phosphine, obtained by rearranging eq 4, was plotted against the cone angle, θ (Figure 5). The points can be fitted with 2 connected straight line segments which join at 136±2°. This has been termed a steric threshold and has been observed for a number of systems. It has been rationalized as arising from the onset of steric effects when the incoming

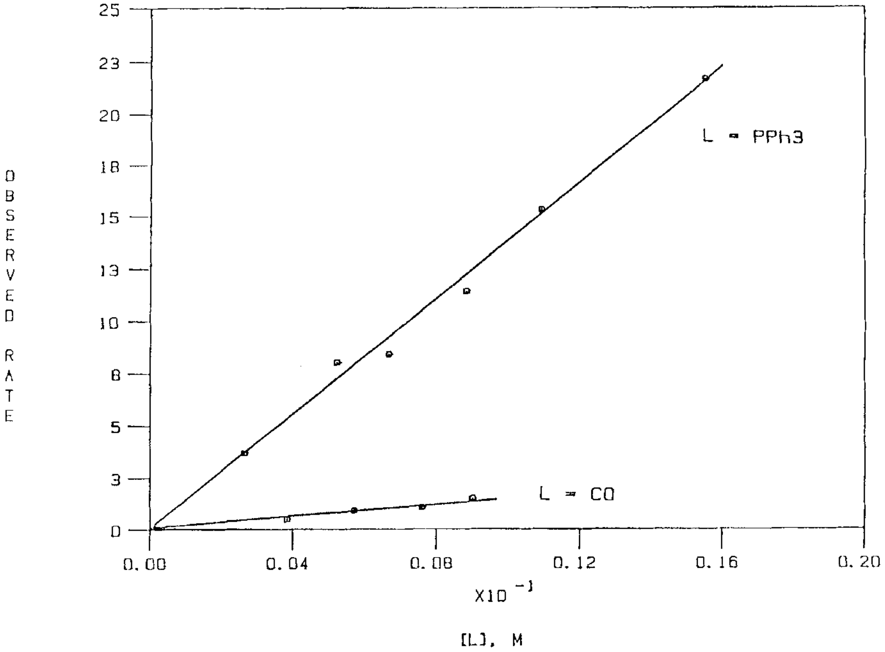


Figure 3 Plot showing the linear dependence of the observed rate constant against PPh_3 concentration (top line) and CO concentration (bottom line) for disappearance of the transient following flash photolysis of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$.

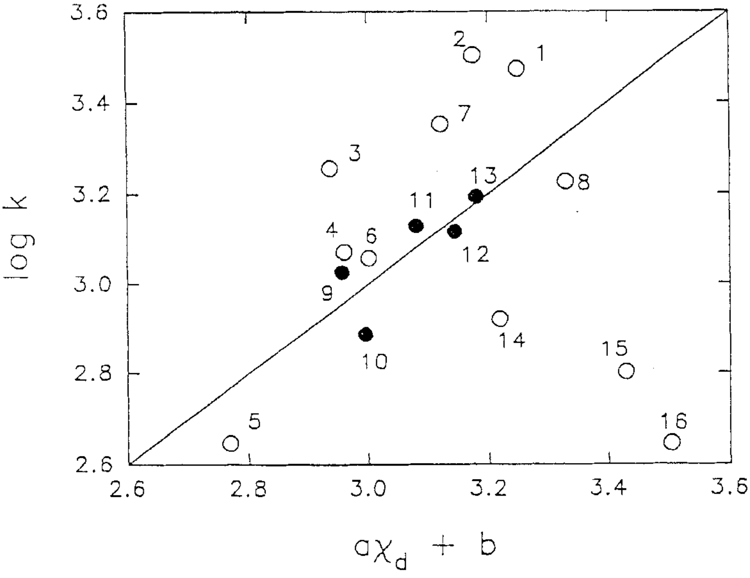


Figure 4 Plot of log k *vs* $a\chi_d$ + b for all phosphine studied. The five isosteric triaryl phosphines used to obtain the regression line are shown as solid circles.

nucleophile is just large enough to interact with the hole at the vacant coordination site. Recent theoretical studies suggest that the absolute steric threshold is much smaller than the apparent steric threshold.[25] This is due not only to the contributions of the van der Waal's repulsive forces but also the contribution of a dispersion energy term. Thus the experimental steric threshold value is not a measure of the size of the coordination vacancy.

Effect of Bound Ligands on the Rate of Reaction

Rate constants for reaction 6 were measured for a variety of substituents in the para position of the benzyl ring to measure the electronic effect of the benzyl ring on the rate.

$$CpFe(CO)(\eta^3\text{-}CH_2C_6H_4\text{-p-X}) + PPh_3 \rightarrow CpFe(CO)PPh_3(\eta^1\text{-}CH_2C_6H_4\text{-p-X}) \quad (6)$$

Experimental rate constants are compiled in Table 2. Examining the rate constants, it is clear that electron donating substituents retard the rate of phosphine addition ($k = 580\ M^{-1}s^{-1}$ for X = OMe) and electron withdrawing substituents speed the rate ($k = 2900\ M^{-1}s^{-1}$ for X = Cl). Application of the Hammett equation produces a plot with a ρ value of + 1.24 (Figure 6). The data suggest that the increased π-donation

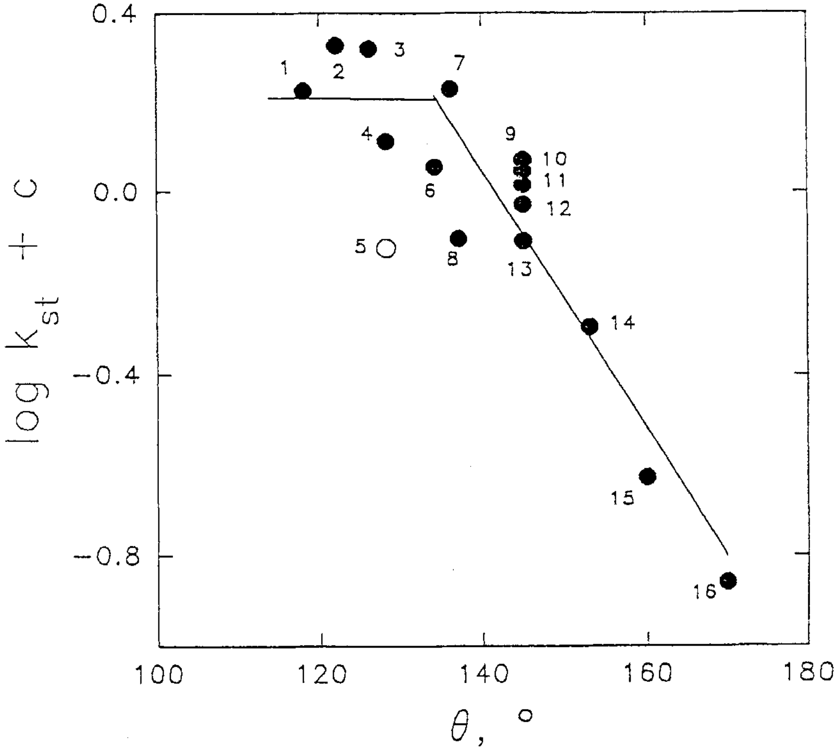


Figure 5 Plot of log k_{st} *vs* θ. A steric threshold of 136 ± 2° was obtained.

Table 2 Reaction rate constants for addition of PPh_3 to $CpFe(CO)(\eta^3\text{-}CH_2C_6H_4\text{-}p\text{-}X)$, X = OMe, Me, H, F, Cl, Br

Compound	k, $M^{-1}s^{-1}$	σ^a
$CpFe(CO)(\eta^3\text{-}CH_2C_6H_4\text{-}p\text{-}OMe)$	$5.8(6) \times 10^2$	-0.27
$CpFe(CO)(\eta^3\text{-}CH_2C_6H_4\text{-}p\text{-}Me)$	$1.05(9) \times 10^3$	-0.17
$CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$	$1.34(5) \times 10^3$	0.0
$CpFe(CO)(\eta^3\text{-}CH_2C_6H_4\text{-}p\text{-}F)$	$2.5(3) \times 10^3$	0.06
$CpFe(CO)(\eta^3\text{-}CH_2C_6H_4\text{-}p\text{-}Cl)$	$2.9(3) \times 10^3$	0.23
$CpFe(CO)(\eta^3\text{-}CH_2C_6H_4\text{-}p\text{-}Br)$	$2.4(2) \times 10^3$	0.23

[a] Hammett σ constants for the para-substituent on the phenyl ring.

from the η^3-benzyl to the metal stabilizes the transient. Since dechelation must occur either prior to or simultaneously with nucleophile attack (see below), increased benzyl-metal π-interaction decreases the rate of ligand addition.

The reaction of $Cp^*Fe(CO)(\eta^3\text{-}CH_2C_6H_5)(Cp^* = C_5Me_5)$ with Lewis base nucleophiles was also examined. The transient is readily produced from the dicarbonyl by flash photolysis. The electronic spectrum of the transient has a λ_{max} of 500 ± 5 nm (Figure 7). Under a CO atmosphere a bimolecular rate constant of 4.4×10^2 $M^{-1}s^{-1}$ was recorded. Reaction with PPh_3 under N_2 proceeds with a bimolecular rate constant of 79 $M^{-1}s^{-1}$. Thus the effect of the Cp* ligand is to enhance the rate of reaction of the intermediate with sterically non-demanding CO and to greatly decrease the rate of reaction with PPh_3. The Cp* ligand is more electron releasing

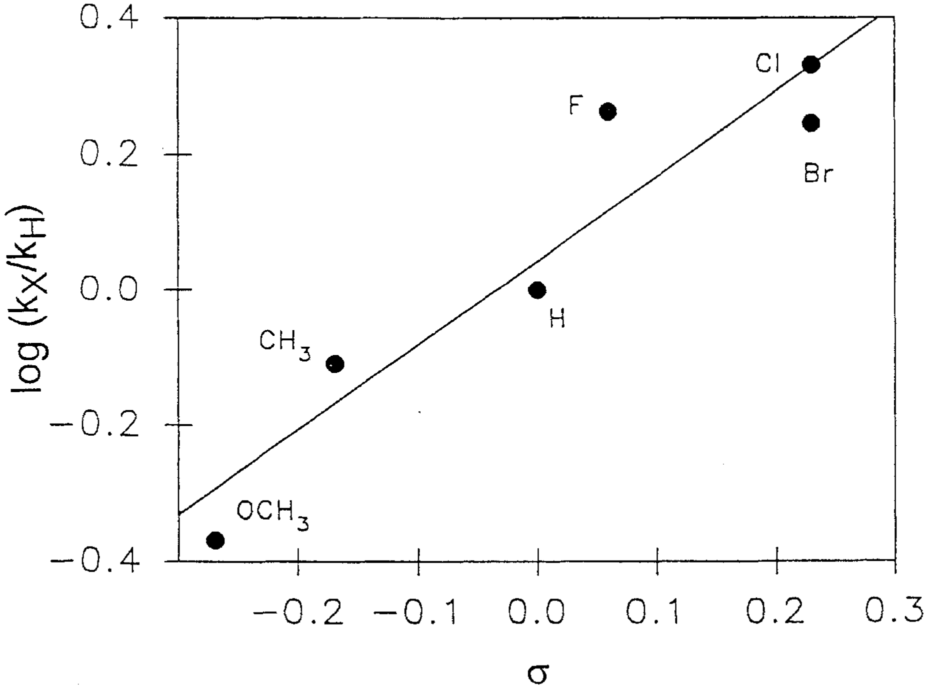


Figure 6 Hammett plot for the reaction of $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ with PPh_3. A ρ value of + 1.24 was obtained from the plot (R = 0.945).

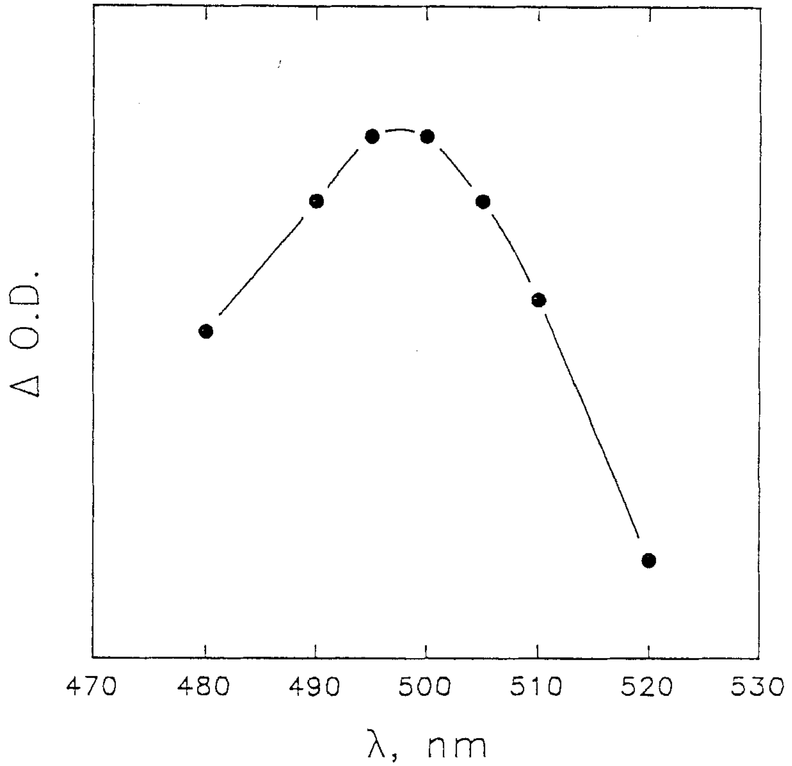
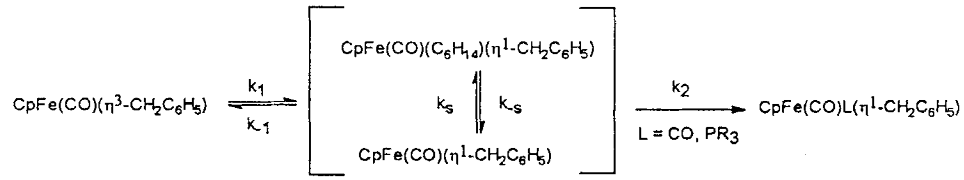


Figure 7 Electronic spectrum of the transient observed following flash photolysis of Cp*Fe(CO)$_2$(η^1-CH$_2$C$_6$H$_5$) in hexane. Data were obtained by measuring the optical density immediately after the flash at several wavelengths. A λ_{max} of 500 ± 5 nm was measured.

than the unsubstituted cyclopentadienyl ligand providing a more electron rich metal. This leads to a weaker benzyl-iron π-interaction. Apparently the larger steric bulk of the Cp* ligand causes increased steric interactions with large incoming ligands such as PPh$_3$, thus moderating the rate of that reaction.

Determination of the Mechanism

Two mechanistic extremes can be imagined that agree with the observed mixed-second-order rate law. One can assume a multistep reaction involving initial dechelation of the benzyl group. This dechelated intermediate would presumably be in rapid equilibrium with the solvento complex. The η^1-species would then add phosphine, in competition with rechelation, to form the product (Scheme 1). Assuming that establishment of the equilibria for the two intermediates is rapid relative to formation of the product, the derived rate law is $R = k_1k_2[CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)][L]/(k_{-1} + k_2[L])$. When $k_{-1} > k_2[L]$, the observed rate law $R = k_{obs}[CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)][L]$ would be observed. A second mechanistic possibility would feature direct attack of the nucleophile at iron in the η^3-benzyl complex (Scheme 2) giving the rate law, $R = k_{obs}[CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)][L]$.



Scheme 1

Scheme 2 $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5) + L \rightarrow CpFe(CO)L(\eta^1\text{-}CH_2C_6H_5)$

Monitoring the reaction in different solvents was performed to try to differentiate between the two mechanisms. Rates of reaction of PPh_3 with $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ in hexane, CH_2Cl_2, THF and acetone are collected in Table 3. The observed rates differ by less than a factor of 3. A strong inhibition of the reaction in better donor solvents would strongly suggest the first mechanism. The lack of an observed effect does not rule out either scheme. The observed variation in rates can be attributed to solvent dielectric differences, etc.

The reaction of $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ in hexane as a function of temperature (10° to 60°C) was studied for various phosphine nucleophiles. Figure 8 shows the resulting Eyring plots which were obtained. All plots exhibited correlation coefficients of less than - 0.999. Activation parameters are collected in Table 4. Definite trends are observed with $\Delta S^\ddagger$ becoming less negative from $P(OPh)_3$ to PPh_3 to PEt_3 to PMe_3 and ΔH essentially constant over the same series. A plot of enthalpy *vs* entropy barriers for the systems studied shows a linear variation (Figure 9). This suggests that the same mechanism prevails for each phosphine nucleophile. An isokinetic temperature of 192 K is measured for this system.

Although the entropy barriers are negative they do not imply a direct nucleophilic attack by the phosphine. The magnitudes of the entropy changes are small and, against expectations, the smaller, more nucleophilic trialkyl phosphines give the least ordered transition states. A stepwise mechanism as shown in Scheme 1 would give linear Eyring plots of ln (k/T) *vs* 1/T.[26] The measured barriers would actually be composite values equal to (ΔS_1° + $\Delta S_2^\ddagger$) and ($\Delta H_1^\circ + \Delta H_2$). The composite

Table 3 Bimolecular rate constants for addition of PPh_3 to $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ in various solvents.

Solvent	Rate, $M^{-1}s^{-1}$
Hexane	$1.34(5) \times 10^3$
CH_2Cl_2	$5.3(5) \times 10^2$
thf	$5.2(5) \times 10^2$
acetone	$1.1(1) \times 10^3$

Table 4 Activation parameters for reaction of phosphine nucleophiles with $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ in hexane.

	$P(OPh)_3$	PPh_3	PEt_3	PMe_3
$\Delta H^\ddagger$, kcal/mol	10.3(0.1)	12.0(0.3)	11.6(0.2)	11.9(0.2)
$\Delta S^\ddagger$, cal/mol-K	-11.3(0.2)	-3.9(0.9)	-4.4(0.5)	-2.3(0.5)

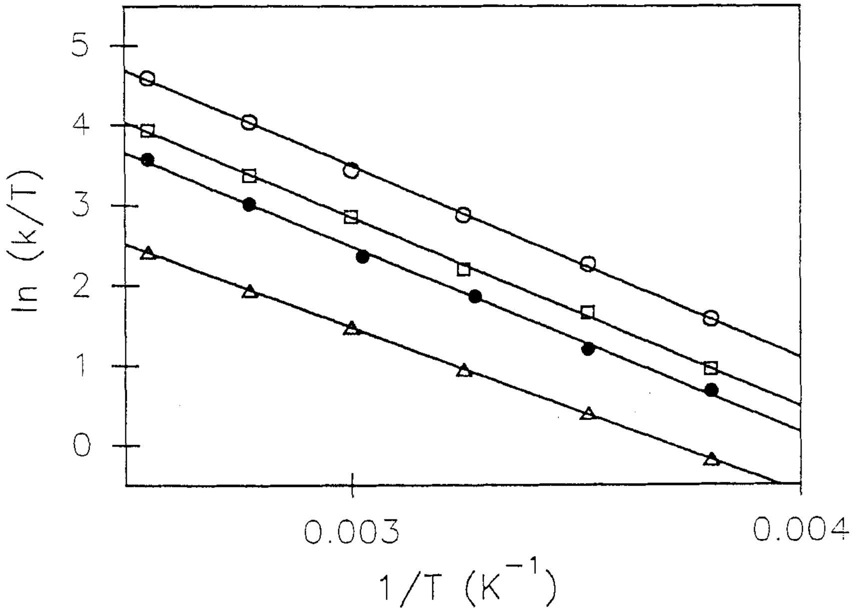


Figure 8 Eyring plots for reaction of CpFe(CO)(η^3-$CH_2C_6H_5$) with PMe_3(O), PEt_3 (□), PPh_3 (●) and $P(OPh)_3$ (△) between 10°C and 60°C.

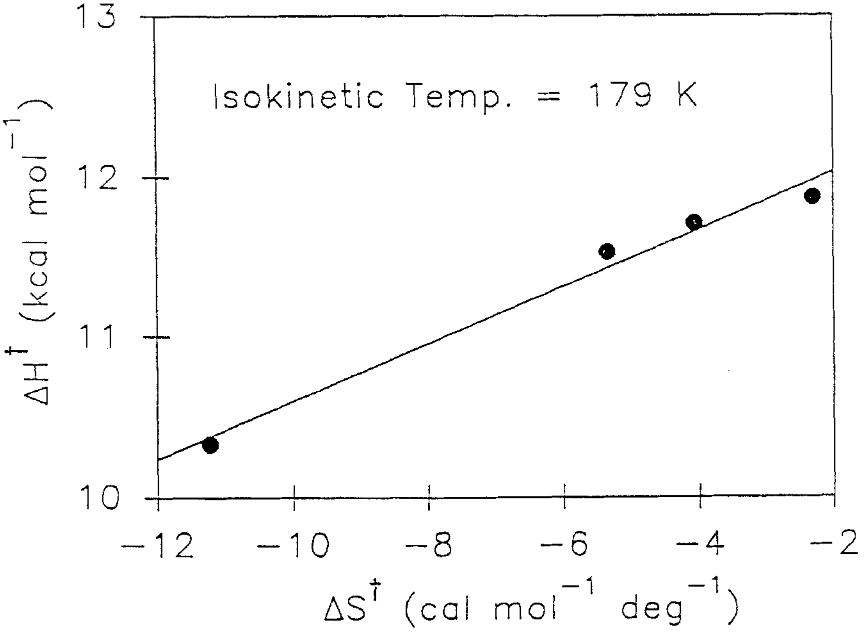


Figure 9 Plot of the isokinetic relationship for CpFe(CO)(η^3-$CH_2C_6H_5$) with the nucleophiles PMe_3, PEt_3, PPh_3 and $P(OPh)_3$. An isokinetic temperature of 192 K was determined.

enthalpy barrier should show little dependence on the character of the nucleophile since $\Delta H_1°$ is constant and is expected to be larger than $\Delta H_2^{\ddagger}$. It is also plausible that the composite entropy barrier could be negative since $\Delta S_2^{\ddagger}$ would be negative. These results suggest that the stepwise mechanism is in operation. This agrees with the work of Brookhart et al. who report NMR evidence for the fleeting existence of the η^1-benzyl complex following the dechelation of the η^3-complex.[12]

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