Nucleophilic Addition of Tertiary Phosphines and Phosphites to Coordinated Cyclobutadiene: A Mechanistic Study

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Tertiary phosphines and phosphites add rapidly and reversibly to the cyclobutadiene ring in $[(C_4H_4)Fe(CO)(NO)(L)]PF_6$ to produce exo phosphonium salts, $[(C_4H_4{\cdot}PR_3)Fe(CO)(NO)(L)]PF_6$. Kinetic studies of this reaction were made in nitromethane solvent with a variety of nucleophiles and nonreacting ligands, L. The cyclobutadiene ring electrophilicity spans a range of about 100 as the ligand L is varied: L = CO > $P(CH_2CH_2CN)_3 \approx P(p\text{-}C_6H_4Cl)_3 > P(p\text{-}C_6H_4F)_3 > As(C_6H_5)_3 \approx P(C_6H_5)_3 > Sb(C_6H_5)_3 \approx P(p\text{-}C_6H_4Me)_3 > P(p\text{-}C_6H_4OMe)_3$. The para-substituted arylphosphines produce an excellent Hammett correlation for the addition of $P(OC_4H_9)_3$. These results provide quantitative information concerning the dependence of π-hydrocarbon activation on the nonreacting ligands and may be useful when designing new systems for synthetic or catalytic purposes. The nucleophilic reactivity follows the order $P(n\text{-}C_4H_9)_3 > P(p\text{-}C_6H_4OMe)_3 > P(p\text{-}C_6H_4Me)_3 > P(C_6H_5)_3 > P(CH_2CH_2CN)_3 > P(OC_4H_9)_3$. This series correlates with Tolman's χ scale. Hammett, Brønsted, and rate-equilibrium constant correlations suggest that bond formation and sp^2 to sp^3 rehybridization is roughly one-third complete in the transition state for the addition reactions.

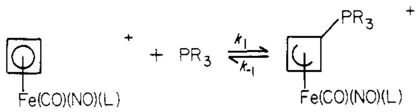
Introduction

It is well-known[1] that by coordination to transition metals π-hydrocarbons can be activated to nucleophilic attack. Reaction of the complexed hydrocarbon with nucleophilic reagents has been utilized in both stoichiometric and catalytic transformations.[2] Neutral complexes of the chromium triad, $[(arene)M(CO)_3]$, have been the most extensively studied,[3] primarily due to their solubility properties and ease of synthesis. However, the hydrocarbon activation is a strong function of the charge on the complex and species such as $[(arene)Mn(CO)_3]^+$ and $[(arene)_2M]^{2+}$ (M = Fe, Ru, Os) are far more electrophilic than $[(arene)M(CO)_3]$, which reacts only with very strong bases. Cationic π-hydrocarbon complexes frequently react with relatively mild bases (amines, alcohols, etc.) and promise to be superior reagents if adequate synthetic procedures and reaction conditions can be formulated.

Nucleophilic addition to coordinated π-hydrocarbons represents an important reaction in organometallic chemistry, but surprisingly little quantitative information of predictive value is available. The factors that determine thermodynamic and kinetic electrophilic character are known only in the most qualitative sense. Likewise, nucleophilic reactivity patterns toward the π-hydrocarbons are poorly understood. Ideally one would like to be able to design a metal complex that would best suit a given problem in synthesis. Before this can be done a detailed mechanistic understanding of the nucleophile–organometallic electrophile combination reaction must be available.

The attack of a nucleophile on an electrophilic complex such as $[(arene)Mn(CO)_3]^+$ can be quite complex mechanistically because attack can occur at the arene, the metal, or coordinated carbon monoxide. Examples of all three possibilities are known. When the thermodynamic product involves attack on the organic ring, the nucleophile is almost always positioned exo to the metal, suggesting direct addition to the ring without prior formation of a metal–nucleophile or M–C(O)–nucleophile intermediate that can convert to product in a concerted manner. Kinetic studies by Kane-Maguire[4] and us[5] support this direct addition mechanism.

Mechanistic studies[4,5] with tertiary phosphine and phosphite nucleophiles have allowed for the first time a quantitative measure of the relative electrophilic character of coordinated π-hydrocarbons. In this paper we report results of a study of reaction 1, which was chosen to examine



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L, PR_3 = CO, $P(CH_2CH_2CN)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$, $P(n\text{-}OC_4H_9)_3$, $P(n\text{-}C_4H_9)_3$, $P(p\text{-}C_6H_4X)_3$ (X = H, F, Cl, CH_3, OCH_3)

the effect of varying the nonreacting ligands. The nonreacting ligand, L, is shown to influence markedly the electrophilicity of the C_4H_4 ring in a predictable manner. The present work, along with previous results, provides a farily extensive series of electrophilic reactivity of π-hydrocarbon complexes. Future work will test the transferability of the order obtained via phosphine addition reactions to that with other types of nucleophiles. If successful, semiquantitative predictions will be possible concerning the feasibility of proposed reactions in synthetic procedures.

The direct combination of an electrophile and a nucleophile is one of the most fundamental types of chemical reactions. Several attempts have been made to understand the intimate mechanism of the reaction with organometallic electrophiles. Based on a large Brøsted slope, Kane-Maguire[6] suggested considerable C–P bond formation in the transition state for reaction 2. Similarly,

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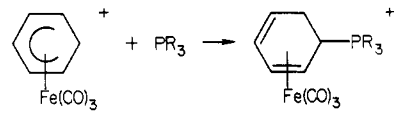

(2)

III

pyridines and anilines give Brønsted slopes near unity for addition to III, and anilines give a Hammett slope $\rho = -2.7$ for variation of X in (p-C_6H_4X)NH_2. Kane-Maguire interpreted these results to mean that the C_6H_7 ring in III is "hard" and the reaction is well advanced in the transition state.

Correlations to Brønsted and Hammett slopes are suggestive but do not necessarily mean a late transition state. It is better to have equilibrium constants for the reactions being studied and to apply the Leffler–Hammond postulate,[7] which assumes that small structural variations in the nucleophile cause a change in the free energy of the transition state that can be written as a linear combination of free energy changes in the reactants and products. This is done below for some of the reactions of $[(C_4H_4)Fe(CO)(NO)(L)]^+$.

Nucleophilic addition to organic electrophiles is of fundamental interest in organic chemistry. Ritchie has shown[8] by his remarkable N_+ correlation that relative nucleophilic reactivity is almost electrophile independent. This suggests an early transition state with electrophile and nucleophile well separated, but this conclusion is at least partly inconsistent with Brønsted slopes of about 0.5 for amine addition to esters.[8] Likewise Bruice found[9] a slope of unity in a plot of log k_1 vs. log K_{eq} for amine addition to Malachite Green. Bernasconi's work[10] with benzylidene Meldrum's acid shows that bond formation to the nucleophile and rehybridization of the sp^2 carbon center in the electrophile need not be balanced in the transition state. Watts and Bunton studied[11] nucleophile addition to ferrocenyl stabilized cations, $FcCRR'^+$, and interpreted their results as meaning little bond formation in the transition state with anionic nucleophiles. Their results with amine and water as nucleophiles are less clear-cut with some data suggesting considerable bond formation while others imply an early transition state. An assessment of the likely transition-state structure for reaction 1 is discussed below. As more information becomes available, it will be very interesting to compare mechanistic features of the "organic" and "organometallic" electrophile–nucleophile combination reactions.

Experimental Section

All solvents were distilled and dried prior to use. Phosphine and phosphite nucleophiles were recrystallized or distilled. Infrared spectra were recorded in acetone and CH_3NO_2 solutions on a Perkin-Elmer 257 spectrophotometer. Proton NMR spectra were recorded on a Varian EM 360 instrument. The cyclobutadiene complexes, $[(C_4H_4)Fe(CO)(NO)(L)]PF_6$, were prepared by procedures very similar to published ones.[12] These complexes react rapidly with phosphines to yield phosphonium ring adducts that are easily isolated.[12]

Table I. IR Spectra of Adducts of $[(C_4H_4)Fe(CO)(NO)(L)]PF_6$ in Nitromethane

L	nucleophile	ν_{CO}/cm^{-1}	ν_{NO}/cm^{-1}
CO		2123, 2098	1880
CO	$P(OBu)_3$	2058, 2006	1767
CO	$P(OMe)_3$	2053, 2000	1760
CO	$P(CH_2CH_2CN)_3$	2067, 2017	1774
CO	$P(p\text{-}C_6H_4OMe)_3$	2053, 2003	1762
CO	$P(C_6H_5)_3$	2050, 2007	1762
CO	PBu_3	2053, 2000	1760
$P(C_6H_5)_3$		2073	1829
$P(C_6H_5)_3$	$P(OBu)_3$	1974	1718
$P(C_6H_5)_3$	$P(OMe)_3$	1969	1712
$P(C_6H_5)_3$	$P(p\text{-}C_6H_4OMe)_3$	1968	1712
$P(C_6H_5)_3$	$P(C_6H_5)_3$	1964	1728
$As(C_6H_5)_3$		2073	1834
$As(C_6H_5)_3$	$P(OBu)_3$	1976	1723
$As(C_6H_5)_3$	$P(OMe)_3$	1970	1720
$As(C_6H_5)_3$	$P(p\text{-tolyl})_3$	1970	1720
$As(C_6H_5)_3$	$P(C_6H_5)_3$	1980	1722
$As(C_6H_5)_3$	$[(C_6H_5)_2PCH_2]_2$	1970	1720
$Sb(C_6H_5)_3$		2070	1832
$Sb(C_6H_5)_3$	$P(OBu)_3$	1977	1723
$Sb(C_6H_5)_3$	$P(C_6H_5)_3$	1978	1728
$P(p\text{-}C_6H_4F)_3$		2076	1830
$P(p\text{-}C_6H_4F)_3$	$P(OBu)_3$	1968	1710
$P(p\text{-}C_6H_4Cl)_3$		2070	1832
$P(p\text{-}C_6H_4OMe)_3$		2073	1828
$P(p\text{-}C_6H_4OMe)_3$	$P(OBu)_3$	1970	1713
$P(p\text{-tolyl})_3$		2070	1825
$P(p\text{-tolyl})_3$	$P(OBu)_3$	1970	1712

The tertiary phosphite adducts, $[(C_4H_4\cdot P(OR)_3)Fe(CO)_2(NO)]PF_6$, were prepared by adding 0.6 mmol of $P(OR)_3$ (R = n-Bu, Me) to a slurry of 0.58 mmol of I in 10 mL of CH_2Cl_2. The reaction mixture quickly became homogeneous and red in color. Addition of pentane deposited a red oil which as thoroughly washed with pentane and dried under N_2. The R = n-Bu product failed to crystallize, but the $P(OMe)_3$ adduct yielded orange crystals that analyzed well for the proposed structure.

Reaction dynamics were followed in nitromethane with a Dionex stopped-flow apparatus thermostated at 25 °C. Most reactions were monitored at 410 or 450 nm. Pseudo-first-order conditions were used with the metal complex being $(1–4) \times 10^{-4}$ M and the nucleophile concentration at least 10 times as large. The pseudo-first-order rate constant, k_{obsd}, was determined at least three times at each of seven or more different nucleophile concentrations. Curve fitting to eq 3 (see Discussion) with use of

$$k_{obsd} = k_1[Nu] + k_{-1} \qquad (3)$$

a relative deviation least-squares minimization gave values of k_1, k_{-1}, and the equilibrium constant $K_{eq} = k_1/k_{-1}$. The correlation coefficients were at least 0.99 for all plots of eq 3.

With tri-n-butylphosphine (PBu_3) as the nucleophile, the rates are very large and k_1 was best determined under second-order conditions. For these experiments PBu_3 and the metal complex were made equal to 2.0×10^{-4} M and the second-order rate constant, k_1, was calculated from the slope of a plot of $1/(A_\infty - A)$ vs. time.

Results

Complexes $[(C_4H_4)Fe(CO)(NO)(L)]PF_6$, where L is CO or a tertiary phosphine, were previously reported by Efraty.[12] These readily react with tertiary phosphines, reaction 1, to yield phosphonium ring adducts[12,13] which can be isolated as crystalline solids. In most cases the

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Table II. Rate Constants for Addition of PR_3 to $[(C_4H_4)Fe(CO)(NO)(L)]PF_6$[a]

L	PR_3	$k_1/M^{-1}\ s^{-1}$	k_{-1}/s^{-1}	K_{eq}/M^{-1}
CO	$P(OBu)_3$	510 ± 20		
$P(C_6H_5)_3$	$P(OBu)_3$	9.8 ± 0.1	0.03 ± 0.015	330 ± 170
$As(C_6H_5)_3$	$P(OBu)_3$	10.0 ± 0.15	0.04 ± 0.015	250 ± 100
$Sb(C_6H_5)_3$	$P(OBu)_3$	6.9 ± 0.15	0.04 ± 0.02	170 ± 90
$P(p\text{-}C_6H_4Cl)_3$	$P(OBu)_3$	23.4 ± 1.0		
$P(p\text{-}C_6H_4F)_3$	$P(OBu)_3$	16.0 ± 0.3	0.04 ± 0.015	400 ± 160
$P(p\text{-}C_6H_4Me)_3$	$P(OBu)_3$	6.6 ± 0.2	0.04 ± 0.015	160 ± 60
$P(p\text{-}C_6H_4OMe)_3$	$P(OBu)_3$	4.9 ± 0.1	0.05 ± 0.01	100 ± 20
$P(CH_2CH_2CN)_3$	$P(OBu)_3$	23.5 ± 0.3		
CO	$P(C_6H_5)_3$	44000 ± 1700		
$P(C_6H_5)_3$	$P(C_6H_5)_3$	1740 ± 70	44 ± 1.3	40 ± 3
$P(C_6H_5)_3$	$P(p\text{-}C_6H_4Me)_3$	6290 ± 70	6.9 ± 0.3	910 ± 50
$As(C_6H_5)_3$	$P(p\text{-}C_6H_4Me)_3$	6940 ± 110	6.5 ± 0.5	1070 ± 100
$Sb(C_6H_5)_3$	$P(p\text{-}C_6H_4Me)_3$	5070 ± 100	8.0 ± 0.4	630 ± 50
$P(C_6H_5)_3$	PBu_3[b]	120000 ± 60000		
$As(C_6H_5)_3$	PBu_3[b]	120000 ± 50000		
$Sb(C_6H_5)_3$	PBu_3[b]	100000 ± 40000		
$P(C_6H_5)_3$	diphos	13000 ± 100	2.3 ± 0.15	5650 ± 400
$P(C_6H_5)_3$	$P(p\text{-}C_6H_4OMe)_3$	11500 ± 500	1.5 ± 0.4	7500 ± 2300
CO	$P(p\text{-}C_6H_4Cl)_3$	7400 ± 100	3.8 ± 0.4	1950 ± 250
CO	$P(CH_2CH_2CN)_3$	1100 ± 40	0.9 ± 0.4	1200 ± 600

[a] 25 °C, CH_3NO_2 solvent. Errors listed are 1 standard deviation. [b] Both first- and second-order conditions used.

adducts (II) were not isolated but were well characterized via IR and NMR spectra. Table I gives the pertinent IR data.

The tertiary phosphite adducts have not been previously reported. They were not observed to undergo an Arbuzov rearrangement to the phosphonate as has been reported for the phosphite adducts of $[(C_6H_6)_2M]^{2+}$ (M = Fe, Ru)[14] and $[(C_6H_6)Rh(C_5Me_4Et)]^+$.[15] The ^1H NMR spectrum of $[(C_4H_4{\cdot}P(OMe)_3)Fe(CO)_2NO]PF_6$ in CH_3NO_2 is similar to that of the phosphine adducts and is assigned as follows: δ 5.77 (t, H-3), 5.17 (s, H-2 and -4), 3.75 (dd, H-1 endo), 4.2 and 4.4 $[-P(OMe)_3]$.

In reaction 1 it is conceivable that the nucleophile could replace the ligand L as well as adding to the cyclobutadiene ring. IR and NMR studies showed clearly that replacement of L by the nucleophile did indeed occur in some cases but at a relatively slow rate that did not interfere with kinetic measurements of the addition step.

The rate and equilibrium constants for reaction 1 are given in Table II.

Discussion

The kinetic data for reaction 1 gave a very good fit to eq 3, which is the standard expression for a simple approach to equilibrium. Equation 3 is consistent with the addition being a direct bimolecular attack on the cyclobutadiene ring. It is also consistent with initial attack on the metal with subsequent migration to the ring. However, there was no kinetic or spectral evidence for metal–nucleophile bonded intermediate species as suggested for PBu_3 addition to cycloheptadienyliron cation.[16] The known[12] exo configuration of the phosphonium ring adducts in reaction 1 argues against a metal-bonded intermediate that can convert to the ring adduct in a concerted manner. The most reasonable mechanism of reaction 1 is simple direct bimolecular addition of the nucleophile.

Table II shows how the electrophilic character of the cyclobutadiene ring depends on the nonreacting ligands. As the ligand L in I is varied the relative reactivity follows the order L = CO > $P(CH_2CH_2CN)_3$ ≈ $P(p\text{-}C_6H_4Cl)_3$ > $P(p\text{-}C_6H_4F)$ > $As(C_6H_5)_3$ ≈ $P(C_6H_5)_3$ > $Sb(C_6H_5)_3$ ≈ $P(p\text{-}C_6H_4Me)_3$ > $P(p\text{-}C_6H_4OMe)_3$. Considering that all the ligands L are neutral, the reduction in k_1 by about a factor of 100 as CO is replaced by PR_3 represents a substantial dependence of electrophilicity on the nonreacting ligands. If this dependence is transferable to other π-hydrocarbon complexes, it will provide a simple way to alter the π-hydrocarbon electrophilicity to meet a synthetic or catalytic requirement. The electrophilic order given above agrees with σ-donor/π-acceptor ratios of PR_3 ligands as determined from ^{13}C NMR shifts in $Ni(CO)_3L$ complexes.[17] Similarly, log k_1 as a function of L with $P(OBu)_3$ as the nucleophile correlates reasonably well with χ values reported by Tolman,[18] which are based on the $\nu_{CO}(A_1)$ stretch in $Ni(CO)_3L$. Figure 1 gives a Hammett plot for $P(OBu)_3$ addition to $[(C_4H_4)Fe(CO)(NO)(P(p\text{-}C_6H_4X)_3)]^+$. The least-squares slope is 1.39, or 1.39/3 = 0.46 per C_6H_4X group, and is relatively large considering the distance of the X group from the reaction site and the attenuation of substituent effects generally seen in arylphosphines.[19] The

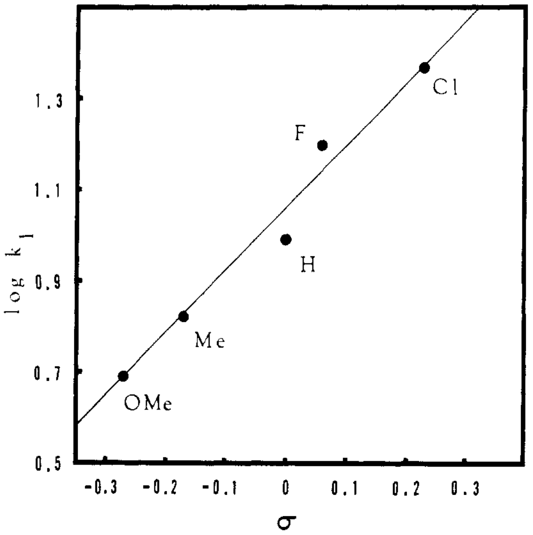

Figure 1. Hammett plot for the addition of $P(OBu)_3$ to $(C_4H_4)Fe(CO)(NO)[P(p\text{-}C_6H_4X)_3]^+$.

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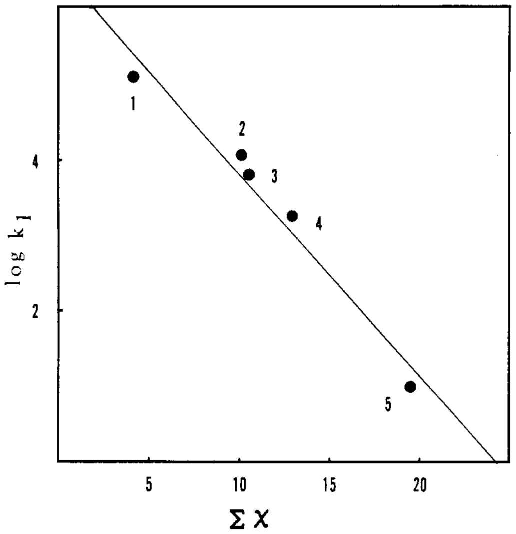

Figure 2. Tolman plot for nucleophile addition to $(C_4H_4)Fe(CO)(NO)[P(C_6H_5)_3]^+$. Number code is as follows: 1, PBu_3; 2, $P(p\text{-}C_6H_4OMe)_3$; 3, $P(p\text{-}C_6H_4Me)_3$; 4, $P(C_6H_5)_3$; 5, $P(OBu)_3$.

relative importance of resonance and inductive effects in determining the observed order is not clear, for a plot using[20] σ^n instead of σ (Figure 1) gives an equally acceptable fit with slope ρ equal to 1.49. Both plots have a correlation coefficient of 0.986. That resonance effects are not primarily important is shown by a lack of correlation to σ^+ values.

Collecting all information available at this time, the following reactivity series with respect to tertiary phosphine addition can be stated:[4,5] $(C_7H_8)Mn(CO)_3^+$ (6600) > $(C_6H_6)_2Fe^{2+}$ (4500) > $(C_4H_4)Fe(CO)_2NO^+$ (750) > $(C_6H_7)Fe(CO)_3^+$ (160) ≈ $(C_6H_6)_2Ru^{2+}$ (150) > $(C_7H_7)Cr(CO)_3^+$ (36) > $(C_6H_6OMe)Fe(CO)_3^+$ (30) > $(C_4H_4)Fe(CO)(NO)(PPh_3)^+$ (27) > $(C_7H_7)M(CO)_3^+$ [M = Mo, W] (23) > $CpFe(CO)_2(C_2H_4)^+$ (2) > $(C_7H_9)Fe(CO)_3^+$ (1.7) > $(C_6H_6)Mn(CO)_3^+$ (1). The numbers are relative reactivities.

The phosphine nucleophiles follow the reactivity order PBu_3 > $P(p\text{-}C_6H_4OMe)_3$ > $P(p\text{-}C_6H_4Me)_3$ > $P(p\text{-}C_6H_5)_3$ > $P(CH_2CH_2CN)_3$ > $P(OBu)_3$. Comparisons to work on other organometallic systems[4,5] suggest that this order of reactivity is at least semiquantitatively transferable to other electrophilic complexes, and this implies that reactivity and selectivity may not be correlated.

A two-point Brønsted plot of $P(C_6H_5)_3$ and $P(p\text{-}C_6H_4OMe)_3$ adding to I (L = $P(C_6H_5)_3$) gives a slope of 0.47. The same nucleophiles reacting with C_2H_5I in acetone and $C_6H_5CH_2Cl$ in benzene/methanol have slopes 0.49 and 0.47, respectively.[21,22] The similarity of the slopes suggest some, but far from complete, bond formation to phosphorus in the transition state of reaction 1. In contrast, nitrogen-donor nucleophiles add to $[(C_6H_7)Fe(CO)_3]^+$ with Brønsted slopes near unity.[4] This was suggested to mean that the π-hydrocarbon is quite "hard". The much smaller slope with phosphine nucleophiles may mean that "softness" (polarizability) of the nucleophile is also important in determining nucleophilicity.

Correlations of k_1 to proton basicity of the nucleophile do not reflect possible π-bonding effects. That purely inductive effects are insufficient to account for the rates is implied by the plot of log k_1 vs. Σχ values of Tolman[18] (Figure 2), which has a slope of −0.27 and a correlation coefficient of 0.98. The Σχ values presumably include both σ and π properties of the phosphine nucleophiles.

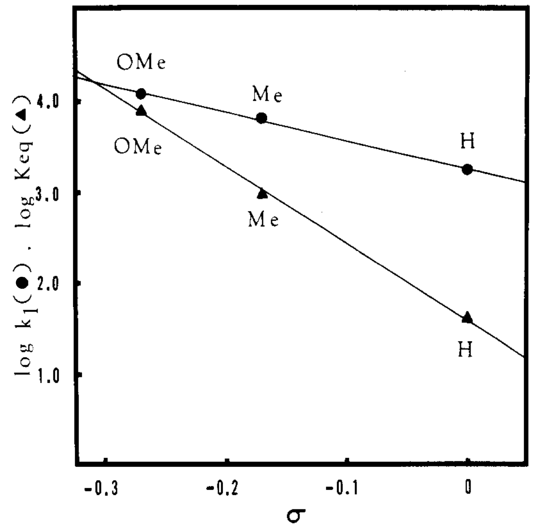

Figure 3. Hammett plots of $P(p\text{-}C_6H_4X)_3$ addition to $(C_4H_4)Fe(CO)(NO)[P(C_6H_5)_3]^+$.

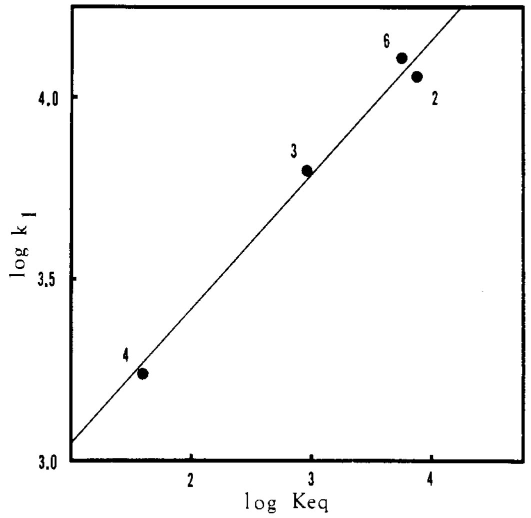

Figure 4. Rate-equilibrium correlation for nucleophile addition to $(C_4H_4)Fe(CO)(NO)[P(C_6H_5)_3]^+$. See Figure 2 for number code; nucleophile 6 is diphos.

Hammett plots of the rate and equilibrium data in Table II are quite instructive. The Hammett slope (ρ_1) for log k_1 in Figure 3 is −1.0 and is almost identical with the slopes for the reaction[21] of $Et_2P(C_6H_4X)$ and C_2H_5I (ρ = −1.1) and that[22] of $P(C_6H_4X)_3$ and $C_6H_5CH_2Cl$ (ρ = −3.5/3 = −1.2). Nitrogen donors usually give larger slopes:[23] $XC_6H_4NMe_2$ + CH_3I (ρ = −3.0); $XC_6H_4NH_2$ + C_6H_5COCl (ρ = −2.7). Anilines adding to $[(C_6H_6OMe)Fe(CO)_3]^+$ give ρ = −2.7.[4] Larger Hammett slopes with nitrogen donors do not imply greater bond formation in the transition state but probably merely reflect[19] decreased conjugation between the phosphorous atom and the substituent compared to the nitrogen analogues.

If the Leffler–Hammond postulate[7] applies to reactions like (1), the best way to determine transition-state structure is to examine the relative sensitivities of k_1 and K_{eq} to structural variations in the nucleophile. Unfortunately,

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it is often experimentally impossible to measure both rate and equilibrium constants. However, for reaction 1 this was possible in some cases, as shown in Figures 3 and 4. Figure 4, which includes diphos and triarylphosphine nucleophiles, has a slope of 0.38, which compares favorably with that derived from Figure 3, $\partial \log k_1/\partial \log K_{eq} = \rho_1/\rho_{eq} = 0.36$. This suggests that bond formation and sp^2 to sp^3 rehybridization is approximately one-third complete in the transition state. This view is supported by the similarity noted above of the Brønsted and Hammett slopes for reaction 1 and S_N2 attack on the sp^3 carbon in C_2H_5I. A reexamination[24] of reaction 2 data also supports this view. However, recent work[5] on $P(C_6H_5)_3$ addition to $[(C_6H_6)_2M]^{2+}$ (M = Fe, Ru, Os) was interpreted in terms of a late transition state, so the intimate mechanism of reactions such as (1) and (2) remains somewhat uncertain. Phosphine addition to "organic" carbocations is being studied in this laboratory to determine the validity of Ritchie's N_+ equation[8] for phosphine nucleophiles and to provide a basis for comparison of coordinated π-hydrocarbon and carbocation electrophiles.

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Registry No. I (L = CO), 43175-64-0; I (L = $P(C_6H_5)_3$), 43140-27-8; I (L = $As(C_6H_5)_3$), 43140-28-9; I (L = $Sb(C_6H_5)_3$), 43140-29-0; I (L = $P(p\text{-}C_6H_4Cl)_3$), 79200-93-4; I (L = $P(p\text{-}C_6H_4F)_3$), 79200-95-6; I (L = $P(p\text{-}C_6H_4Me)_3$), 79200-97-8; I (L = $P(p\text{-}C_6H_4OMe)_3$), 79200-99-0; I (L = $P(CH_2CH_2CN)_3$), 79201-01-7; II (L = CO, R = OBu), 79201-02-8; II (L = $P(C_6H_5)_3$, R = OBu), 79201-03-9; II (L = $As(C_6H_5)_3$, R = OBu), 79201-04-0; II (L = $Sb(C_6H_5)_3$, R = OBu), 79201-05-1; II (L = $P(p\text{-}C_6H_4Cl)_3$, R = OBu), 79215-36-4; II (L = $P(p\text{-}C_6H_4F)_3$, R = OBu), 79201-06-2; II (L = $P(p\text{-}C_6H_4Me)_3$, R = OBu), 79201-07-3; II (L = $P(p\text{-}C_6H_4OMe)_3$, R = OBu), 79201-08-4; II (L = $P(CH_2CH_2CN)_3$, R = OBu), 79215-37-5; II (L = CO, R = C_6H_5), 53062-44-5; II (L = $P(C_6H_5)_3$, R = C_6H_5), 79215-38-6; II (L = $P(C_6H_5)_3$, R = $p\text{-}C_6H_4Me$), 79215-39-7; II (L = $As(C_6H_5)_3$, R = $p\text{-}C_6H_4Me$), 79215-40-0; II (L = $Sb(C_6H_5)_3$, R = $p\text{-}C_6H_4Me$), 79201-09-5; II (L = $P(C_6H_5)_3$, R = Bu), 79215-41-1; II (L = $As(C_6H_5)_3$, R = Bu), 79215-42-2; II (L = $Sb(C_6H_5)_3$, R = Bu), 79215-43-3; II (L = $P(C_6H_5)_3$, PR_3 = diphos), 79215-44-4; II (L = $P(C_6H_5)_3$, R = $p\text{-}C_6H_4OMe$), 79215-45-5; II (L = CO, R = $p\text{-}C_6H_4Cl$), 67324-50-9; II (L = CO, R = CH_2CH_2CN), 79215-46-6.

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Role of the Trichlorostannate Ligand in Homogeneous Catalysis. Mechanistic Studies of the Carbonylation of Phenylplatinum(II) Complexes

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^{31}P NMR studies show that the complexes *trans*-$[Pt(SnCl_3)PhL_2]$ (L = PPh_3 or $PMePh_2$) react with carbon monoxide by an initial, rapid displacement of the trichlorostannate ligand to yield *trans*-$[PtPh(CO)L_2]^+SnCl_3^-$. Further reaction to produce *trans*-$[Pt(SnCl_3)(COPh)L_2]$ occurs slowly in the absence of free CO (L = PPh_3 or $PMePh_2$) by initial nucleophilic attack of $SnCl_3^-$, but in the presence of excess CO an alternative route involving phosphine dissociation (L = PPh_3 only) operates. Comparative studies with other anions have led to a reinterpretation of the role of the trichlorostannate ligand in carbonylation and decarbonylation reactions of organoplatinum(II) complexes.

Introduction

The insertion of carbon monoxide into platinum–carbon bonds has been the subject of a number of studies,[1-6] and, in particular, the carbonylation of *trans*-$[PtXR^1(PR_3)_2]$ (X = halide; R^1 = alkyl or aryl) complexes has received considerable attention.[4-6] Kinetic studies have indicated that both associative and dissociative pathways are involved,[4] and the operation of the associative reaction path has been shown to be sensitive to the electronic character of the migrating organic group.[5] Several reaction intermediates have been identified, and the involvement of the $[PtXR^1(CO)(PR_3)]$ complexes, produced by phosphine dissociation, has been elucidated.[6]

Recently it has been shown[7] that decarbonylation of *trans*-$[PtCl(COR)(PPh_3)_2]$ (R = alkyl or aryl) complexes is promoted by tin(II) chloride, though the role of $SnCl_2$ was not well understood.

We have investigated the carbonylation of *trans*-$[Pt(SnCl_3)PhL_2]$ (L = PPh_3 or $PMePh_2$) and the reverse reaction with a view to discovering how the trichlorostannate ligand promotes the carbonyl insertion, or aryl migration, process.

Experimental Section

The complexes *trans*-$[PtClRL_2]$ (R = Ph or COPh; L = PPh_3 or $PMePh_2$) were prepared by displacement of 1,5-cyclooctadiene from the analogous platinum diolefin complexes.[8] The *trans*-

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