using free cobalt complex in the sample compartment and solutions of complex plus ligand in the reference compartment.

Calculation of Thermodynamic Results. The changes in absorbance of the system with addition of various amounts of ligand can be analyzed to simultaneously deduce the equilibrium constant and ($\epsilon_C - \epsilon_A$). ϵ_C and ϵ_A are the values for the molar absorptivities of the 1:1 complex and free acid, respectively. The method of calculation involves simultaneous solution of K^{-1} and ($\epsilon_C - \epsilon_A$) using a computer solution of the Rose–Drago equation.[24-28] For each acid–base pair a series of simultaneous equations are solved and displayed graphically as plots of K^{-1} vs. ($\epsilon_C - \epsilon_A$) to allow a visual assessment of the quality of the data in addition to the statistical parameters obtained from the calculation. The reader is referred to ref 26 for a useful discussion of the technique. The enthalpies and entropies for complex formation were determined from the temperature dependence of the equilibrium constant using a least-squares routine.

Because of the very large amount of data collected in this type of work it is necessary to condense it to a manageable form which still allows the reader to assess its quality. Table II (supplementary material) summarizes the data as follows: for each equilibrium constant determination (i.e., one acid–base pair at a given temperature) the equilibrium constant is reported along with the conditional standard deviation for K and the ratio of the marginal standard deviation to the conditional standard deviation. This information will allow the reader to appreciate the nature of the K^{-1} vs. ($\epsilon_C - \epsilon_A$) plots without the necessity of reproducing all of the plots.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

Registry No. $CF_3Co(bae)(Me_2SO)$, 61522-63-2; $CF_3Co(bae)(THT)$, 61522-64-3; $CF_3Co(bae)(py)$, 61522-65-4; *p*-$MeOC_6H_4Co(bae)(pip)$, 61522-66-5; *p*-$MeOC_6H_4Co(bae)(py)$, 25793-78-6; $C_6H_5Co(bae)(py)$, 41659-59-0; *p*-$FC_6H_4Co(bae)(py)$, 61522-67-6; $CH_2ClCo(bae)(py)$, 61543-15-5; $CH_3Co(bae)(py)$, 18115-79-2; $CF_3Co(bae)$, 61527-77-3; *p*-$MeOC_6H_4Co(bae)$, 41659-50-1; $C_6H_5Co(bae)$, 41686-71-9; *p*-$FC_6H_4Co(bae)$, 61522-68-7; $CH_2ClCo(bae)$, 61522-69-8; $CH_3Co(bae)$, 41744-14-3; Co(bae), 15744-72-6.

Supplementary Material Available: Table II, giving all measured equilibrium constants, conditional standard deviations, and ratios of marginal to conditional standard deviations (1 page). Ordering information is given on any current masthead page.

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(8) Abbreviations for ligands used in this article are as follows: THT, tetrahydrothiophene; Et_3N, triethylamine; DMA, *N,N*-dimethylacetamide; DMTA, *N,N*-dimethylthioacetamide; THF, tetrahydrofuran; Me_2SO, dimethyl sulfoxide; py, pyridine; pip, piperidine; bae, *N,N'*-bis(acetylacetonato)ethylenediimine; $(dmg)_2$, bis(dimethylglyoximato).
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Kinetics of Oxidative Addition to Iridium(I) Complexes[1]

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The effect of the ligand L on the rate of trans addition of CH_3I to *trans*-$Ir(CO)ClL_2$ has been investigated. The tertiary phosphine ligands L were chosen to determine the effects of electronic modifications, the effect of substituent position of the substituted triphenylphosphine, effects of a series of alkyl-substituted phosphine ligands in which the number and size of the alkyl groups is varied, and the effects of stepwise change in a phenyl-substituted phosphine in which the number of substituted phenyl groups is changed from 0 to 3. The use of various types of σ constants in Hammett linear free energy relationships is discussed. Application of substituent constants derived for substituents attached to phosphorus for cases where reaction does not involve direct attack on phosphorus to the data yields a linear relationship between log k and $\sum\sigma^{ph}$ with a slope of -2.27 and a correlation coefficient of 0.99.

Introduction

The kinetics of oxidative addition reactions of transition metal complexes with d^8 and d^{10} electron configurations has received considerable attention in recent years. The impetus for these investigations has been to gain a greater understanding of the electronic and steric factors influencing this reaction which is a vital step in the functioning of many of these compounds as homogeneous catalysts. Following the report[3] on the effects of the halide on the rates of oxidative addition of H_2, O_2, and CH_3I to $Ir(CO)X(Ph_3P)_2$, several investigators cited evidence,[4] although largely qualitative, that seemingly minor changes in the phosphine ligand caused large differences in the reactivity of the complexes. This evidence suggested that inclusion of electron-donating groups in the phosphine ligand enhanced the reactivity of the complexes toward oxidative addition. A kinetics study by Douek and Wilkinson[5] on the analogous $Rh(CO)ClL_2$ (L = Ph_3P, (p-$CH_3OC_6H_4)_3P$, and (p-$FC_6H_4)_3P$) provided further support for this proposed behavior. However, Strohmeier and Onada's[6] investigation of the kinetics of the reversible addition of H_2 to $Ir(CO)ClL_2$ (L = tertiary phosphine) revealed no apparent relationship between the rate of addition and the electronic properties of the phosphine ligands. Studies of the rate of oxygenation of a series of $Ir(CO)ClL_2$ complexes enjoyed reasonable success in correlating the properties of para-substituted triphenylphosphine ligands as measured by Hammett σ constants and the oxygenation rate.[7]

Hydrogen and oxygen are known to undergo cis addition to $Ir(CO)XL_2$, whereas, methyl iodide undergoes trans addition. Thus, while there had been several studies on the effect that the ligand L had on the rate of cis oxidative addition reactions to $Ir(CO)XL_2$, no corresponding studies had been conducted to determine the effects of the phosphine ligand on the rate of trans addition. Halpern and Chock[3] found that the rate of addition of H_2 and O_2 follows the order $I^- > Br^- > Cl^-$ for the halide ligands, while for CH_3I addition, the order was reversed. Against this background, we felt it would be pertinent to investigate the influence of the phosphine ligand on trans addition and undertook, in late 1971, a study of the reaction between methyl iodide and $Ir(CO)ClL_2$ (L = tertiary phosphine).

The series of phosphine ligands to be studied were chosen to determine the effects of (a) purely electronic modifications via use of para-substituted triphenylphosphines, (b) a stepwise change from 0 to 3 in the number of substituted phenyl groups in triphenylphosphine, (c) substituent position in the substituted triphenylphosphine, and (d) successive replacement of phenyl groups in the tertiary phosphine by alkyl groups.

When our investigation was nearly completed, Ugo and co-workers[8] published a paper on the effects of the phosphine ligand on methyl iodide and benzyl halide addition. Since that time several additional kinetic studies of methyl iodide addition for a limited number of phosphines have been reported.[9,10] The authors of these later reports have not attempted to find a quantitative relationship between reaction rates and electronic properties of the phosphines. We now choose to publish the results of our study inasmuch as the number of complexes investigated is more extensive and, more importantly, because we believe we have used a superior method of correlating the results which hopefully will lead to more meaningful interpretations of future studies on the effects of phosphine ligands on the oxidative addition reactions of other d^8 and d^{10} complexes.

Table I. Second-Order Rate Constants for the Reaction *trans*-$IrCl(CO)L_2 + CH_3I \rightarrow Ir(CH_3)ClI(CO)L_2$

Complex	L	T, °C	k_2, $M^{-1}\ s^{-1}$	Rel rate (25 °C)
I	(p-$FC_6H_4)_3P$	25	8.54×10^{-5}	6
II	(p-$BrC_6H_4)_3P$	25	1.68×10^{-5}	1.2
III	(p-$CH_3C_6H_4)_3P$	20	8.83×10^{-3}	
		25	1.32×10^{-2}	910
		30	1.77×10^{-2}	
IV	(p-$CH_3OC_6H_4)_3P$	20	1.42×10^{-2}	
		25	2.53×10^{-2}	1750
		30	3.08×10^{-2}	
V	$(C_6H_5)_3P$	25	2.67×10^{-3}	185
		30	3.17×10^{-3}	
		35	3.59×10^{-3}	
VI	(p-$ClC_6H_4)(C_6H_5)_2P$	25	4.49×10^{-4}	31
VII	(p-$ClC_6H_4)_2(C_6H_5)P$	25	9.32×10^{-5}	6.5
VIII	(p-$ClC_6H_4)_3P$	25	1.44×10^{-5}	1.0
		30	2.12×10^{-5}	
		35	3.83×10^{-5}	
IX	(m-$CH_3C_6H_5)_3P$	25	2.55×10^{-3}	175
		30	2.93×10^{-3}	
		35	4.29×10^{-3}	
X	(o-$CH_3C_6H_5)_3P$	25	No reaction	
XI	$CH_3(C_6H_5)_2P$	25	1.77×10^{-2}	1220
XII	$C_2H_5(C_6H_5)_2P$	20	1.06×10^{-2}	
		25	1.36×10^{-2}	940
		30	1.67×10^{-2}	
XIII	$(C_2H_5)_2(C_6H_5)P$	20	8.35×10^{-3}	
		25	1.15×10^{-2}	830
		30	1.5×10^{-2}	
XIV	$(CH_3)_2(C_6H_5)P$	25	5×10^{-2}	3470[a]

[a] From ref 9.

Experimental Section

Measurements. Infrared spectra of solids were recorded in KBr disks by a Perkin-Elmer Model 337 spectrophotometer and in CH_2Cl_2 solution by a Beckman Model 12 spectrophotometer. Ultraviolet-visible spectra were recorded by a Beckman Model Acta V spectrophotomer.

Materials. Hydrated iridium trichloride purchased from Engelhard Industries, Newark, N.J., was used in the preparation of all complexes. All solvents were of reagent grade and were purified according to methods of Fieser and Fieser[11] and stored over molecular sieve. Prior to use they were deoxygenated by freeze-degassing three times. Reagent grade methyl iodide was washed with 10% aqueous sodium thiosulfate, dried over molecular sieve, distilled under nitrogen, and stored over mercury. The tertiary phosphines $(C_6H_5)_3P$, (m-$CH_3C_6H_4)_3P$, and (o-$CH_3C_6H_4)_3P$ were purchased and purified by recrystallization prior to use. The phosphines $(C_2H_5)(C_6H_5)_2P$, $(C_2H_5)_2(C_6H_5)P$, (p-$FC_6H_4)_3P$, (p-$ClC_6H_4)_3P$, (p-$ClC_6H_4)_2(C_6H_5)P$, (p-$BrC_6H_4)_3P$, (p-$CH_3OC_6H_4)_3P$, and (p-$ClC_6H_4)(C_6H_5)_2P$ were prepared by reaction between PCl_3 and $C_6H_5PCl_2$ or $(C_6H_5)_2PCl$ with the appropriate Grignard reagent. The iridium complexes were prepared by standard procedures.[12,13]

Kinetic Measurements. The kinetics of the reactions

$$Ir(CO)ClL_2 + CH_3I \rightarrow Ir(CO)ClIL_2(CH_3)$$

where L = a tertiary phosphine were followed in dry benzene by measuring the rate of disappearance of the absorption band of the iridium(I) complex around 25 000 cm^{-1}. An approximate 100-fold excess of methyl iodide was used, producing pseudo-first-order kinetics.

Preparations of the complexes for rate determinations were done with the rigorous exclusion of oxygen. All samples and solutions used in the rate determinations were prepared in a glovebag under a positive pressure of purified nitrogen.

A 1.852 M stock solution of methyl iodide and a 5×10^{-3} to 5×10^{-4} M stock solution of the iridium(I) complex were prepared and placed in a constant-temperature bath and allowed to reach thermal equilibrium. One milliliter of the methyl iodide stock solution was pipetted into a 5-mL volumetric flask and the flask filled to the mark with stock solution of the complex. After thorough mixing, the resulting solution was placed in a 1-cm Vycor cuvette with ground-glass stoppers and placed in the thermostatically controlled cell holder. The absorbance was recorded as a function of time at λ_{max}. The reactions were followed for a minimum of 3 half-lives. For each complex an additional determination was performed to observe the appearance of an isosbestic point. In all cases an isosbestic point was observed in the neighborhood of 30 000 cm^{-1} and was maintained throughout the reaction, eliminating the possibility of side reactions. Also, thin-layer chromatography on silica gel G (benzene eluent) data was obtained at the conclusion of each kinetic determination. In all cases only a single product could be detected.

The reaction was found to obey second-order kinetics, rate = $k_2[Ir(CO)ClL_2][CH_3I]$, for all ligands studied. This is in agreement with other studies.[3,8-10] The concentration of the methyl iodide was assumed to be constant. A standard least-squares determination was used to obtain the best fit of the data points, log $[Ir(CO)ClL_2]$ vs. time. Measurement of the kinetics at several temperatures allowed calculation of activation parameters for the reaction. The results of the kinetic measurements are presented in Tables I and II. We find excellent agreement, in those cases where identical complexes were studied, between our data and those reported by other authors[8-10] except when L = (p-$FC_6H_4)_3P$ and (p-$ClC_6H_4)_3P$. However, it may

Table II. Activation Parameters for the Reaction *trans*-$IrCl(CO)L_2 + CH_3I \rightarrow Ir(CH_3)ClI(CO)L_2$

Complex	ΔH_a, kcal/mol	ΔS_a,[a] eu	Complex	ΔH_a, kcal/mol	ΔS_a,[a] eu
I	17.0[b]	−20[b]	VIII	17.1	−22
III	12.1	−28	IX	11.5	−32
IV	15.3	−26	XII	8.1	−31
V	6.2	−51	XIII	11.9	−28

[a] At 25 °C. [b] From ref 8.

be noted that our results for these complexes yield a smaller deviation from the Hammett free energy relationship.

Results

The kinetics of reaction 1 was studied for a series of ligands,

$$Ir(CO)ClL_2 + CH_3I \rightarrow Ir(CH_3)(CO)ClIL_2 \qquad (1)$$

L, where L is a tertiary organophosphine. Under the experimental conditions the reactions went to completion with the formation of only one isomer. On the basis of previous investigations,[4a,8] the products were assumed to be the result of trans addition. (Because of the low concentration of the adduct in the samples used in the kinetic determinations, it was not possible to obtain far-infrared spectra with sufficient resolution of the peaks in the 200–400-cm^{-1} region to make structural assignments. In several instances, the reactions were carried out on a larger scale and the isolated product was shown to be the trans isomer.) The possibility of side reactions was eliminated by the observation of an isosbestic point at 30 000 cm^{-1} which was maintained throughout the reactions.

A summary of the kinetic data and activation parameters is given in Tables I and II. Examination of the data shows that a general trend of increasing reaction rates is paralleled by increasing electron-donating ability of the phosphine ligands.

Discussion

In addition to the limited number of quantitative studies which had been done when our work began, progress in understanding the effects of organophosphine ligands on the reactivity of d^8 and d^{10} complexes has been further hampered by the lack of a suitable means of relating the data. For nearly 40 years organic chemists have benefited from the Hammett equation in the pursuit of quantitative structure–reactivity relationships. Unfortunately, a direct transfer of the results from organic systems to coordination compounds is not possible. The difficulty is that σ constants have, of necessity, been separately evaluated for aromatic and aliphatic systems. In an investigation of complexes, the need is to have a single scale of σ constants which can be used to correlate the effects of tertiary phosphine ligands containing only aryl or alkyl groups and those containing both aryl and alkyl groups. While considering possible solutions to this problem we came across a series of papers by Kabachnik[14-16] which have lain largely unnoticed in the chemical literature. Kabachnik showed that the Hammett equation was applicable to a wide variety of aryl- and alkyl-substituted phosphorus acids when the substituent constant, σ^{ph}, specific to substituents bonded to phosphorus was used. The substituent constants, σ^{ph}, were determined by use of the Hammett equation from measurement of the ionization constants of organophosphorous acids in water and 50% aqueous alcohol. Hypophosphorous acid was chosen as the reference compound (i.e., σ^{ph}(for H) = 0) and ρ, the slope, was defined as 1 for the ionization of phosphorous acids of the type $RR'PO_2H$. The substituent constant represents the value for a single substituent, R or R′, attached to a phosphorus atom. The substituent constant for a particular phosphorus compound is the sum of all individual substituents attached to the phosphorus. Kabachnik felt these substituent constants would be applicable in all cases where the reaction does not involve direct attack on the phosphorus atom.

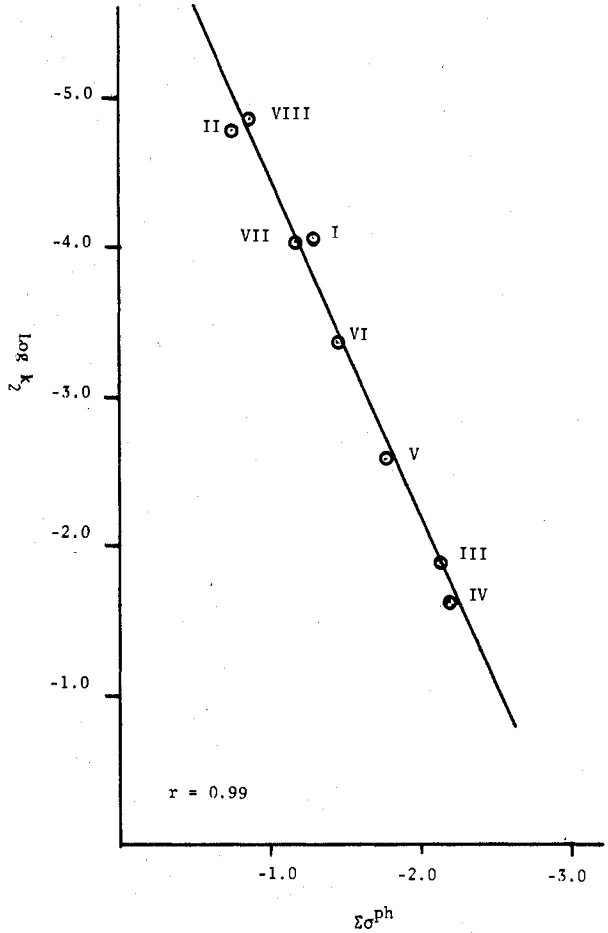


Figure 1. Plot of log k_2 vs. $\sum\sigma^{ph}$ at 25 °C for complexes I–VIII.

It appeared to us that the results of Kabachnik's investigation were precisely what we needed. The phosphorus is in an essentially tetrahedral bonding environment both in the metal complexes and in the organophosphorous acids and in both cases the electronic effects of the organic groups are being transmitted through phosphorus to the reactive site of the molecule.

Davis and Graham[17] studied the kinetics of the addition of methyl iodide to a series of π-cyclopentadienyl–carbonyl-phosphine complexes of cobalt(I) where the phosphine was $CH_3(C_6H_5)_2P$, $(CH_3)_2(C_6H_5)P$, $(C_6H_5)_3P$, or $(C_6H_{11})_3P$. We found a correlation between the second-order rate constant (log k_2) and the sum of the substituent constants,[16] $\sum\sigma^{ph}$, provided the value for the tricyclohexylphosphine complex was omitted. As will be seen later, deviation from the Hammett relationship is apparently due to steric effects of this very bulky ligand.

Thus encouraged, we chose complexes I–VIII (Table I) for investigation. For this series the steric effects are considered to be constant and any change in reaction rate attributed solely to electronic effects of the substituents. A linear relationship was found when log k_2 was plotted vs. $\sum\sigma^{ph}$ with a slope of −2.27 and correlation coefficient r = 0.99, Figure 1. Complexes V–VIII when L = $(p\text{-}ClC_6H_4)_n(C_6H_5)_{3-n}P$ where n is varied from 3 to 0 verified that the substituent constants were additive for this system. The increase in the number of unsubstituted phenyl groups resulted in the expected corresponding increase in reaction rate.

In order to consider the effects and importance the position of the substituent on the phenyl ring has on the rate of methyl iodide addition, complexes IX and X were prepared. Complex

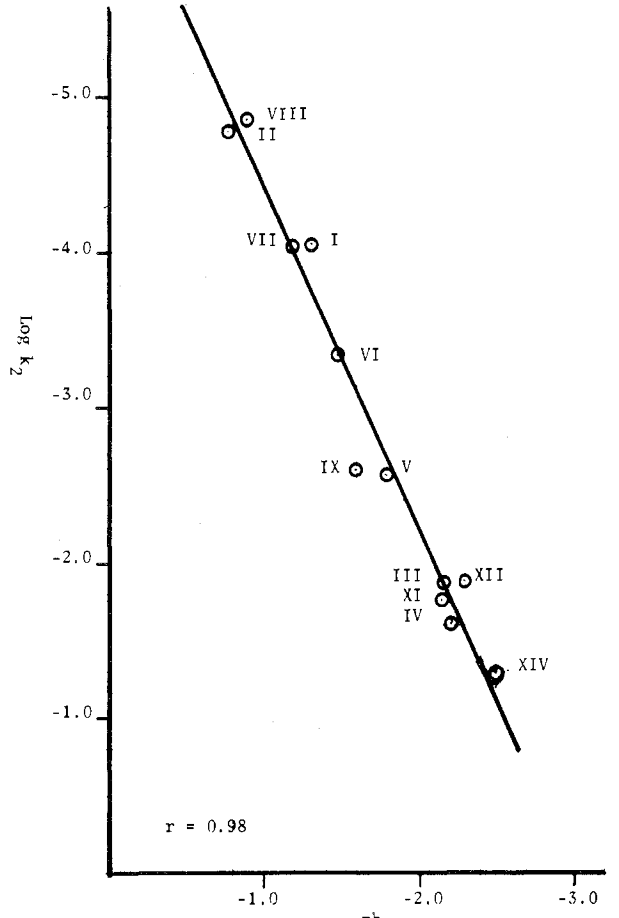


Figure 2. Plot of log k_2 vs. $\sum\sigma^{ph}$ at 25 °C for complexes I–XIV.

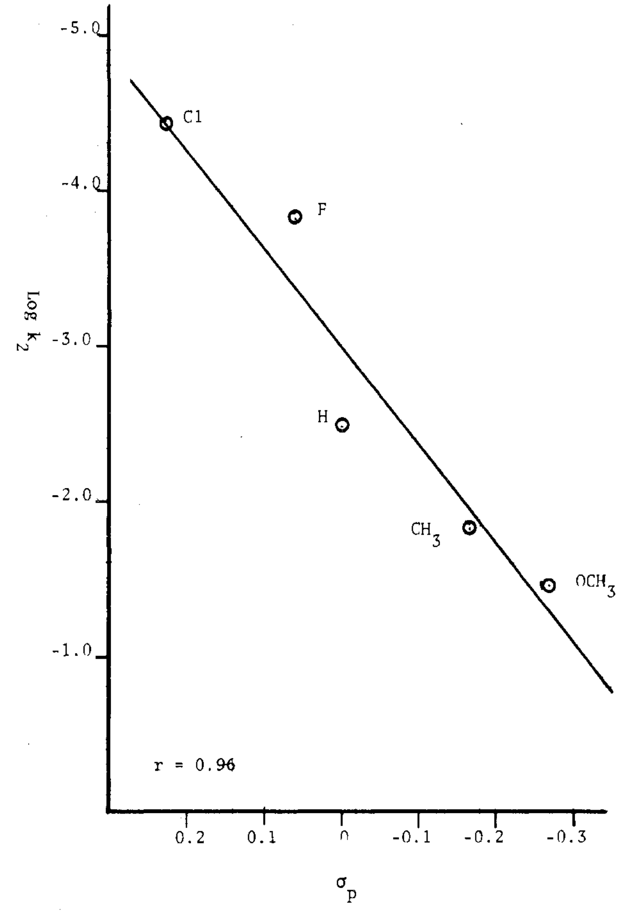


Figure 3. Plot of log k_2 vs. σ_p at 25 °C for data reported in ref 8 for the reaction $Ir(CO)Cl[(p\text{-}XC_6H_5)P]_2 + CH_3I \rightarrow Ir(CO)(CH_3)ClI[(p\text{-}XC_6H_5)_3P]_2$ (X = Cl, F, H, CH_3, OCH_3).

X exhibited no measurable reaction after 48 h. This lack of reactivity is attributed to steric factors. X-ray crystallographic study shows considerable crowding and steric interference around the iridium atom,[18] thus, preventing effective approach of methyl iodide. A model of the *m*-tolylphosphine complex (complex IX) suggests a steric effect might also have been expected; however, it should be much less pronounced than for the *o*-tolylphosphine. Since the *m*-tolyl complex obeys the Hammett relationship (Figure 2), it may be concluded that the change in steric effects upon moving the substituent from the para to the meta position is negligible.

A series of alkyl-substituted phosphines were next chosen for investigation. This series was designed to include complexes in which the number of alkyl groups would be varied from 0 to 3. The series of methyl-substituted phosphines was originally chosen, but a lack of success in preparing the dimethylphenyl- and trimethylphosphine complexes finally led to the investigation of complexes XI–XIII. The order of ligand dependence was found to be $(CH_3)(C_6H_5)_2P > (C_2H_5)(C_6H_5)_2P > (C_2H_5)_2(C_6H_5)P$. This order differs from that predicted solely from consideration of ligand basicity. For complex XI (L = $(CH_3)(C_6H_5)_2P$) the observed rate constant is about 6 times greater than the rate constant for complex V (L = $(C_6H_5)_3P$) which is in accord with the prediction of the Hammett relationship using Kabachnik's σ^{ph} constants (see Figure 2). The value from ref 9 for L = $(CH_3)_2(C_6H_5)P$, complex XIV, is included on Figure 2 and exhibits excellent agreement with predicted values. The order of reactivity for complexes XII and XIII is opposite that expected. The rate of methyl iodide addition for XII (L = $(C_2H_5)(C_6H_5)_2P$) and XIII (L = $(C_2H_5)_2(C_6H_5)P$) was 5 and 4.5 times greater, respectively, than for V. In addition to the order reversal, the rate enhancement for both ligands is less than that predicted. Complex XII deviates from the Hammett equation best-fit line by 20% and the deviation is 150% for complex XIII. Thus it would appear from this reaction series that a methyl group and a phenyl group are comparable in their steric requirements, whereas ethyl and presumably higher alkyl groups exhibit increasing steric interference.

Relationship to Other Studies. As we were finishing our study of the alkyl phosphines, Ugo and co-workers[8] reported kinetic data for the addition of methyl iodide to seven iridium(I) complexes all of which we included in our study. For most complexes studied mutually (complexes I, III, IV, V, VIII, XII, and XIII), the deviations between the two sets of results are within experimental error. Ugo attempted to relate the rate of reaction to Hammett σ_p constants for the five trisubstituted arylphosphines included in his investigation (Figure 3). The correlation coefficient of 0.96 for his data can be improved significantly ($r = 0.99$) and with smaller deviations from the best-fit line by use of σ^{ph} constants (Figure 4).

There have been two accounts of the effects of the phosphine ligands on the addition of oxygen to iridium(I) complexes. A satisfactory correlation is obtained ($r = 0.98$) for a plot of log k_2 vs. $\sum\sigma^{ph}$ for the data reported by Mercer[19] (Figure 5). In contrast to the results obtained for the addition of methyl iodide, the rates of addition of oxygen to complexes XII and XIII yield reasonable agreement with values predicted by the Hammett relationship. A less satisfactory correlation ($r = 0.79$) is obtained for the data reported by Vaska[7] for oxygen addition. However, these data include the results for several complexes containing trialkylphosphine ligands including tricyclohexylphosphine. Since the deviations increase with

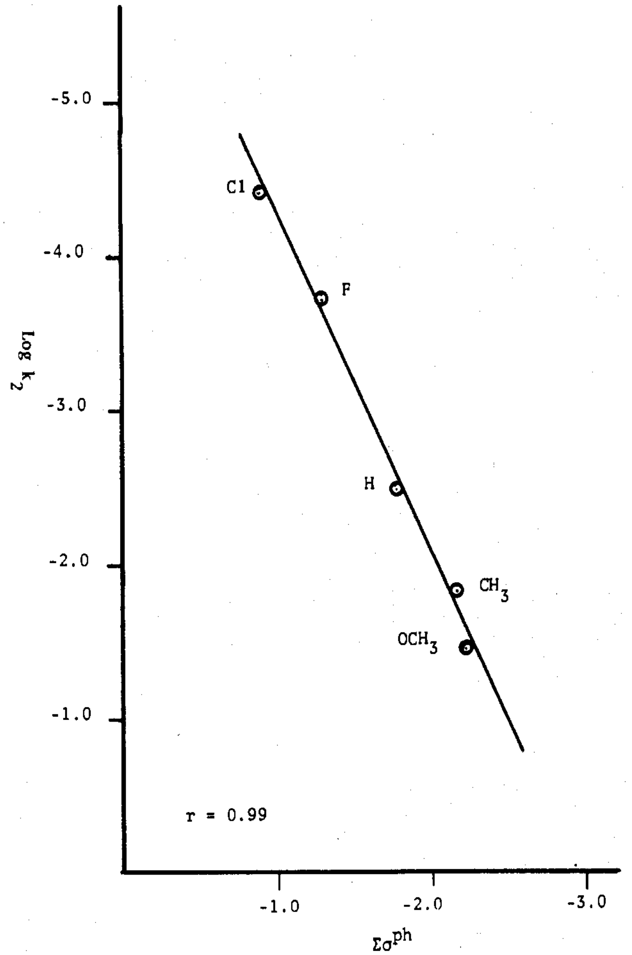


Figure 4. Plot of log k_2 for data in Figure 3 vs. $\sum\sigma^{ph}$.

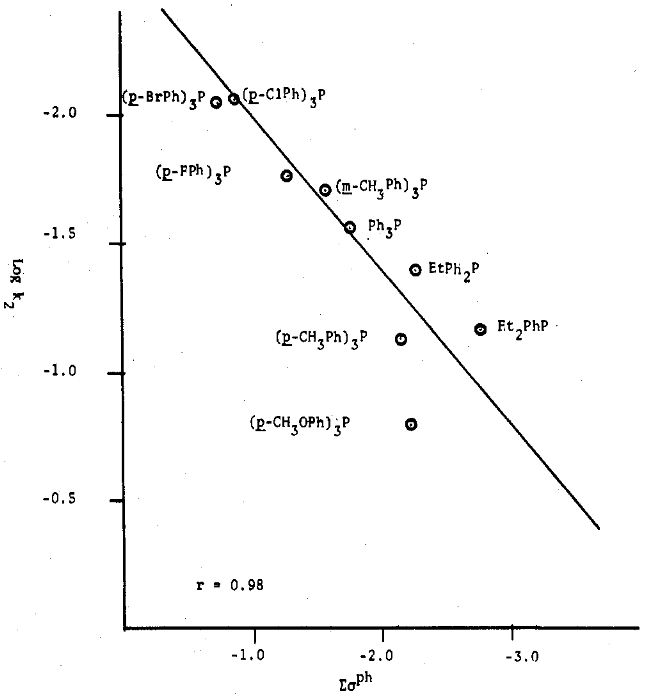
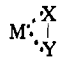


Figure 5. Plot of log k_2 vs. $\sum\sigma^{ph}$ at 25 °C for data reported in ref 16 for the reaction $Ir(CO)ClL_2 + O_2 \rightarrow Ir(CO)ClL_2O_2$.

increasing size of the alkyl groups, they may be attributed to steric effects.

Further supporting evidence for steric interference of the phosphine ligands comes from consideration of the rate of hydrogen addition reported by Strohmeier and Onoda.[6] They also chose several trialkylphosphines as ligands for investigation. Again, it can be observed that the deviations from the Hammett relationship increase with increased bulkiness of the alkyl group. The $\sum\sigma^{ph}$ for the phosphines R_3P (R = *n*-butyl, isopropyl, and cyclohexyl) are approximately the same, while k_2 for the *n*-butylphosphine complex is about 50 times that of the isopropylphosphine complex and greater than 100 times that of the tricyclohexylphosphine complex.

Detailed consideration of possible transition states for oxidative addition to square-planar iridium(I) complexes has been given by other investigators.[8,9,20] The solvent dependence of the reaction is well substantiated and the activation parameters determined in this study and others are in reasonable agreement. From these and other data both three-centered and linear transition states, **1** and **2**, respectively, have been


1

$M\cdots\cdots X{-}Y$
2

proposed for the wide variety of oxidative addition reactions undergone by iridium(I) complexes including that with methyl iodide. We suggest that attempting to describe the transition state for this large number of different reactions as either **1** or **2** is likely to be unproductive. We prefer instead to visualize a gradation of possible transition states intermediate between **1** and **2**. This view considers the angle between the X–Y bond of the adding molecule (Y may or may not be identical with X) and the original plane of the complex. When this angle is zero, the result is transition state **1**, whereas, if the angle is 90°, transition state **2** results. Intermediate angles are possible and a progression of angles may occur for the range of reactions undergone by iridium(I) complexes. The amount of bending of the CO and halide ligands out of their original plane toward a distorted trigonal-bipyramidal (vs. a square-based pyramidal) transition state would be a function of the angle. The angle and consequently the amount of both bond breaking in the addendum molecule and the extent of formation of the second iridium addendum bond in the transition state may dictate whether the cis or trans isomer is formed as the product.

Evidence favoring this picture of the transition state might be inferred from a plot of activation enthalpies against activation entropies for reactions of *trans*-$IrCl(CO)(Ph_3P)_2$ with a variety of addendums which yield a smooth curved line.[20] While the authors point out that caution should be exercised in interpreting rate trends because of the proximity of the isokinetic temperature to room temperature, they also state that *there exists a blurring of the distinction between transition* states **1** and **2** and that the activation parameters are *not* diagnostic of an oxidative addition mechanism.

Relative to oxygen addition, the more negative slope of the Hammett plot for methyl iodide indicates a more polar transition state. This is consistent with the polar character of methyl iodide and a weakening of the carbon–iodine bond during attack on a carbon by iridium. It is not possible to discern from available data whether this process is accompanied by partial formation of an iridium–iodine bond or results in formation of an intimate ion pair.

However, the results of several groups of investigators[21–23] strongly suggest that a linear transition state with the iodide pointed directly away from the metal atom and the original plane of the complex leading to a solvent-separated ion pair or dissociated ions as would be expected from a true Menschutkin type reaction is unlikely. Collman and Sears[21] clearly showed, via the reactions depicted in eq 2 and 3, that the initial trans addition products are the result of kinetic control and not thermodynamic control. The product of eq 3 is not the thermodynamically favored isomer and can be easily isom-

$$\mathrm{Ir(CO)Cl[(C_6H_5)_2(CH_3)P]_2 + CH_3Br} \\ \rightarrow \mathrm{Ir(CO)(CH_3)ClBr[(C_6H_5)_2(CH_3)P]_2} \qquad (2)$$

$$\mathrm{Ir(CO)Br[(C_6H_5)_2(CH_3)P]_2 + CH_3Cl} \\ \rightarrow \mathrm{Ir(CO)CH_3)BrCl[(C_6H_5)_2(CH_3)P]_2} \qquad (3)$$

erized to the configuration of the product of eq 2. It has also been shown that only $\mathrm{Ir(CO)(SCN)L_2(CH_3)I}$ ($\mathrm{L = (C_6H_5)_3P}$) is formed[22] when $\mathrm{Ir(CO)(SCN)L_2}$ is allowed to react with methyl iodide in the presence of $\mathrm{SCN^-}$; only $\mathrm{Ir(CO)ClL_2(CH_3)I}$ is produced when methyl iodide reacts with Vaska's compound in the presence[22] of $\mathrm{Cl^-}$ or in the presence[23] of $\mathrm{^{131}I^-}$. If dissociated ion pairs are formed, external ions should be incorporated in the product. Formation of a solvent-separated ion pair (even if it does not allow incorporation of an external ion) would at least allow thermodynamic rather than kinetic control of the stereochemical course of the reaction.

The distinction between partial iridium–iodine bond formation and formation of an intimate ion pair is a much more difficult problem to resolve. We prefer the partial iridium–iodine bond formation on the following grounds. This view is amenable with the primary arguments of charge transfer used to explain the reversal of reaction rate dependence upon the halide present in the starting iridium(I) complex in the reactions with oxygen and methyl iodide.[9] These same authors suggest deformation from a square plane (presumably toward a trigonal bipyramid) to explain the slower rate of methyl iodide addition to $\mathrm{Ir[(C_6H_5)_3P]_3Cl}$ than to $\mathrm{Ir[(C_6H_5)_3P]_2(N_2)Cl}$. If the suggested deformation is common to all of the complexes and were to proceed *without* sufficient iridium–iodine interaction to preserve the bonding site, thermodynamic control of the stereochemistry would be expected, which is contrary to the observed results. This view would also be consistent with the observation by Stieger and Kelm[24] that the sensitivity to solvent polarity of the oxidative addition reaction is less than that of the Meuschutkin reaction. The transition state proposed here is similar to what we interpret Ugo[8] meant by a polar asymmetric three-centered transition state.

Conclusions

Electronic changes in the phosphine ligands of $\mathrm{Ir(CO)ClL_2}$ (L = tertiary organophosphine) can cause dramatic changes in the reactivity of the complexes toward oxidative addition reactions. For reaction with methyl iodide a change in the substituent groups of tertiary phosphines can effect changes of approximately 3.5×10^3 in the second-order rate constants. Through the use of σ^{Ph} constants, it is possible to apply the Hammett equation to complexes containing aryl, alkyl, and mixed aryl–alkyl organophosphines. For oxidative addition reactions of the square-planar iridium(I) complexes investigated there are pronounced steric effects. These steric effects are dependent upon both the phosphine ligand and the covalent molecule added. In the case of methyl iodide addition, ethyl or larger alkyl groups on the phosphine ligand cause significant deviation from the Hammett equation, whereas, with the smaller oxygen molecule, no deviations are observed with ethyl-substituted phosphines although larger alkyl groups will cause deviations.

Registry No. I, 23408-46-0; II, 61616-96-4; III, 28195-56-4; IV, 34054-03-0; V, 15318-31-7; VI, 61587-69-7; VII, 61587-70-0; VIII, 34275-84-8; IX, 34054-06-3; XI, 15318-32-8; XII, 23723-99-1; XIII, 15842-03-2; $\mathrm{CH_3I}$, 74-88-4.

References and Notes

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