3.40, 7.85, 8.00, 8.98, 10.9, 13.9, 14.8 μm.

Anal. Calcd for $C_{17}H_{16}N_4S_3O_4{\cdot}2H_2O$: C, 43.24; H, 4.23; N, 11.86; S, 20.38. Found: C, 42.86; H, 4.39; N, 11.77; S, 20.50.

Treatment of 4a with Water. A suspension of 100 mg of **4a** in 2 mL of distilled water was heated on a steam bath for 30 min. The resulting clear solution was then left overnight at room temperature. The white solid which precipitated during this period was filtered, weighed (55 mg), and identified as benzenesulfonamide, mp 152–154 °C.

Treatment of 4a with 1 M HCl. On treatment of 200 mg of **4a** with 1 M HCl, a white solid precipitated which was filtered, washed with brine, and crystallized from ethanol to give 60 mg of **7**: mp 131.5–133 °C; NMR [$(CD_3)_2S{=}O$] δ 8.04 and 7.78 (aromatic), 2.52 (NH); IR (KBr) 2.98, 3.50, 6.89, 7.78, 7.94, 8.97, 10.6, 13.2, 14.6 μm.

Anal. Calcd for $C_{12}H_{13}N_3S_2O_2{\cdot}2H_2O$: C, 43.50; H, 5.13; N, 12.68; S, 19.38. Found: C, 43.66; H, 4.46; N, 12.62; S, 19.06.

Treatment of 4b with Water. A 50-mg sample of **4b**, dissolved in 1 mL of water, was heated for 30 min on a steam bath. The solution was then left at room temperature for several hours. The white solid, which precipitated, was filtered, weighed (20 mg), and identified as benzenesulfonamide, mp 151–153 °C.

Acknowledgment. This investigation was supported by PHS Research Grant Nos. CA15,771 and CA18,839 from the National Cancer Institute.

Registry No. 2, 28464-34-8; **3a**, 63823-93-8; **3b**, 64051-75-8; **3c**, 63823-94-9; **3d**, 69069-47-2; **4a**, 69069-49-4; **4b**, 69069-50-7; **7**, 69069-51-8; **8**, 69069-53-0; trichlorophosphazosulfonyl chloride, 14700-21-1; PCl_5, 10026-13-8; sulfamoyl chloride, 7778-42-9; morpholine, 110-91-8; piperidine, 110-89-4; diethylamine, 109-89-7; triethylamine, 121-44-8; trimethylamine, 75-50-3; pyridine, 110-86-1; benzenesulfonamide, 98-10-2.

References and Notes

(1) H. R. Allcock, *Chem. Rev.*, **72**, 315 (1972).
(2) E. M. Smolin and L. Rapoport, "S-Triazines and Derivatives", Interscience, New York, 1959.
(3) T. Moeller and R. L. Dieck in "Preparative Inorganic Reactions", Vol. 6, W. L. Jolly, Ed., Wiley-Interscience, New York, 1971, p 63.
(4) T. Moeller and A. Ouchi, *J. Inorg. Nucl. Chem.*, **28**, 2147 (1966).
(5) O. Glemser, *Z. Naturforsch. B*, **31**, 610 (1976).
(6) D.-L. Wagner, H. Wagner, and O. Glemser, *Chem. Ber.*, **108**, 2469 (1975); **109**, 1424 (1976).
(7) H. Wagner, R. Mews, T.-P. Lin, and O. Glemser, *Chem. Ber.*, **107**, 584 (1974).
(8) R. L. McKenney, Jr., and N. R. Fetter, *J. Inorg. Nucl. Chem.*, **30**, 2927 (1968).
(9) A. Failli, M. A. Kresge, C. W. Allen, and T. Moeller, *Inorg. Nucl. Chem. Lett.*, **2**, 165 (1966).
(10) A. J. Banister and B. Bell, *J. Chem. Soc. A*, 1659 (1970).
(11) For preliminary communication, see T. J. Maricich and M. H. Khalil, *Chem. Commun.*, 195 (1967).
(12) A. V. Kirsanov, *J. Gen. Chem. USSR (Engl. Transl.)*, **22**, 101 (1952).
(13) β-Sulfanuric chloride gives the same isomer of **2** as α.

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Kinetics and Mechanism of Oxidative Addition of Aryl Iodides to Iridium(I) Complexes

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Received July 7, 1978

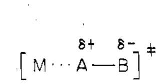
The kinetics of oxidative addition of aryl iodides to *trans*-$IrCl(CO)L_2$ (L = tertiary phosphine) are governed by a two-term rate law, $R = \{k_1 + k_2[ArI]\}[Ir]$, similar in form to the equation describing substitution reactions of square-planar complexes. The second-order path is decreased by added phosphine. Electron-withdrawing groups in either the aryl halide or the complex enhance the rate of reaction. Linear free energy relationships were found between k_2 and the Hammett σ_p for substituents in the aryl iodide ($\rho = +0.6$) and between k_2 and the Kabachnik $\sum\sigma^{ph}$ for substituents on the phosphine ($\rho = +0.4$). A two-step mechanism is suggested for the second-order path involving predissociation of the phosphine ligand. These data are compared with prevailing ideas concerning the mechanisms of oxidative addition reactions of d^8 square-planar complexes.

Introduction

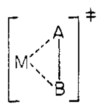
Since the classic study of Chock and Halpern,[3] the reactions of Vaska's compound *trans*-$IrCl(CO)(PPh_3)_2$ and its analogues have held a central position in efforts to elucidate the mechanism of oxidative addition of small molecules to d^8 transition-metal complexes (1). In spite of the intense activity

$$trans\text{-}IrCl(CO)L_2 + AB \rightarrow trans\text{-}IrCl(A)(B)(CO)L_2 \quad (1)$$
$$L = \text{triphenylphosphine}$$

in this field numerous questions remain unanswered. The nature of the transition state remains a controversial topic. Both linear (I) and three-center (II) transition states have been

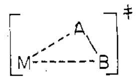


I



II

suggested. The original proposal[3–6] that homopolar oxidants (A = B) react via a symmetrical transition state (I) whereas polar oxidants (A ≠ B) react via a linear transition state (II) has recently been modified.[7] An unsymmetrical three-center transition state (III) which may be regarded as a gradation



III

between forms I and II has been proposed. Evidence favoring this view was adduced from the findings[6] that the activation parameters for the addition of a variety of molecules of Vaska's compound could be accommodated by a single smooth curve, with an isokinetic temperature. Many authors[4,7–10] have cited evidence that inclusion of electron-releasing functional groups in the coordinated phosphine ligands enhances the reactivity of the complex toward oxidative addition. The analogous rhodium(I) complex $RhCl(CO)(PAr_3)$ was shown to behave similarly.[11] However, no great reactivity differences were found for the addition of H_2 to *trans*-$IrCl(CO)L_2$ (L = tertiary phosphine).[4]

The influence of electronic factors in the addend molecule has previously been investigated for the addition of substituted benzyl chlorides.[4] We have recently shown[12] that aryl halides may be added to Vaska's compound and its analogues. In this system the bond activated by the iridium(I) complex is an aromatic carbon–iodide linkage, which should be expected to be particularly sensitive to the electronic effects of substituents

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in the aryl moieties. This paper describes the results of a kinetic study of the addition of aryl iodides to iridium(I) complexes with particular emphasis on the electronic effects induced by substituents on the aryl nucleus as well as by substituents on the phenyl groups of coordinated phosphine. As discussed below, this system shows striking mechanistic differences from all previously studied oxidative addition systems involving Vaska-type complexes and small molecules.

Experimental Section

Materials. $IrCl(CO)(PPh_3)_2$ and derivatives with para-substituted triphenylphosphines were prepared by a method similar to that of Collman and Kang.[13] Upon refluxing of $IrCl_3.3H_2O$ (500 mg, 1.4 mmol) with the appropriate phosphine (7 mmol) in DMF, addition of methanol and cooling yielded 70–93% of yellow crystalline products which were washed with cold methanol and vacuum dried at 100 °C. The compounds analyzed satisfactorily. Iridium(III) complexes, $IrClI(Ar)(CO)(PAr'_3)_2$, formed by addition of ArX to Vaska's compound or its PAr'_3 analogue, were synthesized and characterized as described previously.[12] The solvent, 1-methylnaphthalene, was vacuum distilled over $LiAlH_4$ and degassed before use.[4]

Kinetics. The reactions of Vaska's complex and its analogues with aryl iodides proceed at a measurable rate only at elevated temperatures in the region of 150 °C. (Rates of reaction with aryl chlorides and bromides are considerably slower and were not investigated.) Under these conditions solutions of iridium(I) species are extremely sensitive to oxidation by traces of oxygen, and therefore all samples were prepared and the kinetic measurements conducted in an argon atmosphere.

The reaction vessel consisted of a spectrophotometric cell fused to one arm of a T-shaped tube with the upright of the T parallel to the cell. The bottom end of the T was sealed and the free arm was fitted with a ground glass stopper. Under argon one reactant solution was injected into the optical cell by means of a calibrated automatic syringe, and the other reactant solution was injected into the upright of the T. The reaction vessel was then sealed with a ground glass stopper lined with Teflon tape. When the reactants had attained thermal equilibrium in the apparatus described below, the reaction was initiated by inverting the reaction vessel to ensure rapid and complete mixing of the two reagents and the solution transferred to the optical cell part of the vessel.

The spectrophotometer consisted of a Beckman DU monochromator on which was mounted the cell compartment and a Gilford 220 photomultiplier. The output signal of the photomultiplier was recorded on a Telrad chart recorder. The cell compartment consisted of a cell holder equipped with copper tubing to facilitate the circulation of oil from a thermostatically heated oil bath. On each side of the hot section a sheet of asbestos insulating material (1 cm thick) and a hollow brass plate (1 cm thick), through which cooling water was continuously pumped, served to protect the monochromator and photomultiplier from heat damage. With this apparatus, temperatures of the reaction mixture in the range 140–160 °C could be maintained constant to within ±1 °C.

The reaction was monitored by following the change in absorbance of the characteristic peak of the iridium(I) species at 387 nm. All reactions were conducted using a large excess of aryl iodide to ensure pseudo-first-order conditions. A large excess of PPh_3 was used in reactions to study the influence of phosphine. Plots of log $(A_t - A_\infty)$ against time were linear for at least 3 half-times, and rate constants were obtained by linear regression analysis of the data. Correlation coefficients were usually better than 0.99.

Results

Under the experimental conditions, reaction 1 proceeds to completion. Plots of the pseudo-first-order constant obtained for the reaction of *trans*-$IrCl(CO)(PPh_3)_2$ with six different aryl iodides at six different concentrations were found to be linear with a significant nonzero intercept (2), in all but one case. The error limits on the value of the intercept are large, but the existence of an added-independent reaction path is statistically significant, particularly in view of the agreement of the value of k_1 obtained from $k_{obsd}/[ArI]$ plots with the value obtained from studies of the dependence on phosphine concentration (vide infra). Values of k_1 and k_2 are listed in Table I, together with the value of the Hammett σ coefficient for the appropriate functional group on the aryl nucleus. With the exception of the methoxy substituent, which shows a large deviation, rate constants for the second-order path obey a Hammett-type linear free energy relationship (Figure 1). The slope of this line yields a value of $\rho = +0.6$ for the Hammett reaction coefficient.

$$k_{obsd} = k_1 + k_2[ArI] \qquad (2)$$

Table I. Kinetic Data for the Oxidative Addition Reaction of *trans*-$[IrCl(CO)(PPh_3)_2]$ with Aryl Iodides[a,b]

ArI	10^4k_1/ s^{-1}	$10^3k_2/M^{-1}$ s^{-1}	σ(Hammett)
C_6H_5I	0.37 ± 0.15	4.05 ± 0.013	0.00
p-BrC_6H_4I	0.32 ± 0.18	5.72 ± 0.050	0.27
p-ClC_6H_4I	0.35 ± 0.33	5.03 ± 0.050	0.22
p-$CH_3C_6H_4I$	0.45 ± 0.20	3.17 ± 0.020	−0.17
m-$CH_3C_6H_4I$	0.50 ± 0.40	3.83 ± 0.020	−0.07
p-$CH_3OC_6H_4I$	0.32 ± 0.52	6.33 ± 0.055	−0.11

[a] $[IrCl(CO)(PPh_3)_2] = 5 \times 10^{-4}$ M. [b] Reaction temperature 158 °C.

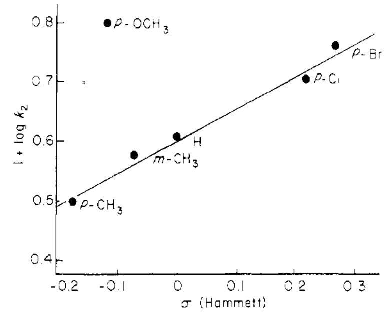


Figure 1. Plot of log k_2 vs. σ(Hammett) for the reaction of *trans*-$[IrCl(CO)(PPh_3)_2]$ with aryl iodides.

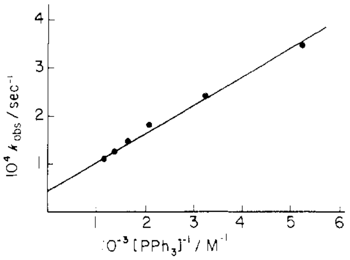


Figure 2. Influence of added PPh_3 on the rate of reaction of *trans*-$[IrCl(CO)(PPh_3)_2]$ with iodobenzene.

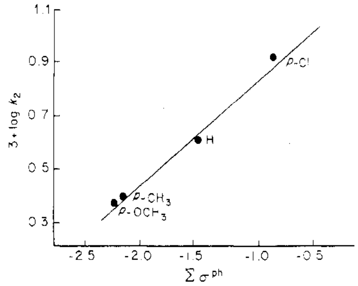


Figure 3. Plot of log k_2 vs. $\sum\sigma^{ph}$ for the reaction of *trans*-$[IrCl(CO)(P(p\text{-}ZC_6H_4)_3)_2]$ with *m*-iodotoluene.

Preliminary investigations showed that in the presence of large amounts of free PPh_3, reaction 1 for L = PPh_3, was almost completely inhibited. (The rate was, however, too small to measure accurately.) This appears to be the first time that such behavior has been observed in oxidative addition of $IrCl(CO)L_2$, and more quantitative kinetic measurements were performed. The results are presented graphically in Figure 2 for the oxidative addition of iodobenzene to *trans*-IrCl-

Table II. Kinetic Data for the Oxidative Addition Reaction of *trans*-[$IrCl(CO)(P(p\text{-}ZC_6H_4)_3)_2$] with *m*-Iodotoluene[a,b]

Z	$10^4 k_1$/ s^{-1}	$10^3 k_2$/M^{-1} s^{-1}	$\Sigma\sigma^{ph}$
CH_3	0.83	2.50	−2.16
Cl	0.83	8.50	−0.87
OCH_3	0.67	2.17	−2.22
H	0.50	3.83	−1.44

[a] [$IrCl(CO)(P(p\text{-}Z\text{-}C_6H_4)_3)_2$] = 5×10^{-4} M. [b] Reaction temperature 158 °C.

$(CO)(PPh_3)_2$. The rate constant varies inversely with the concentration of phosphine, and in addition a statistically significant intercept was found (3). Within the error limits,

$$k_{obsd} = k_1 + k_3/[PPh_3] \tag{3}$$

this value was identical with the value of k_1 found for the reaction without added PPh_3. It should be noted that no reaction between PPh_3 and iodobenzene was observed after 36 h at 165 °C, so that the possibility of the rate retardation being due to a side reaction of this kind may be eliminated.

The influence of substituents on the phenyl rings of the phosphine ligands was investigated by measuring the rates of the reactions of *trans*-$IrCl(CO)[P(p\text{-}ZC_6H_4)_3]_2$ with *m*-iodotoluene (Table II). In all cases a two-term rate law (2) was obeyed. A linear free energy correlation was found between k_2 and Kabachnik's $\sum\sigma^{ph}$ coefficient[14,15] for the substituent, with a value of $\rho = +0.4$ for the reaction coefficient.

Discussion

From a close examination of the results, a number of conclusions may be derived which highlight the mechanistic differences between the present system and reactions of other addend molecules with Vaska-type complexes.

Rate Law. Oxidative addition reactions of type 1 are usually characterized by simple kinetics, nearly all the reactions reported to date being first order in each reactant. For the reaction of benzyl chloride with *trans*-$IrCl(CO)(PPh_3)_2$, departure from first-order behavior was observed after the initial 10% of the reaction.[4] The present study differs from previously reported systems in two important aspects. The rate-retarding effect of phosphine on reaction 1 may be simply interpreted in terms of the following reaction scheme:

$$IrCl(CO)L_2 + S \overset{K}{\rightleftharpoons} IrCl(CO)L(S) + L \tag{4}$$

$$IrCl(CO)L(S) + ArI \xrightarrow{k} IrClI(Ar)(CO)L(S) \tag{5}$$

$$IrClI(Ar)(CO)L(S) + L \xrightarrow{\text{fast}} IrClI(Ar)(CO)L_2 + S \tag{6}$$

S = solvent molecule

Assuming that the rate-determining step in the mechanism (4)–(6) is the forward reaction (5), i.e., equilibration in (4) is rapid, this reaction path yields the rate expression

$$k_{obsd} = kK[ArI]/(K + [PPh_3]) \tag{7}$$

Together with the addend-independent path, this yields the overall rate equation

$$k_{obsd} = k_1 + kK[ArI]/(K + [PPh_3]) \tag{8}$$

In the region of phosphine concentration that we investigated, it is impossible to differentiate unequivocally between the straight line shown in Figure 2 and the early stages of a levelling-off of the rate to an asymptotic value as predicted by eq 8. It should be noted that if the amount of phosphine added was reduced further it would be difficult to evaluate its actual concentration with accuracy as it would be of a similar order of magnitude as the phosphine released from the complex.

Thus, in the region investigated, we may safely apply the inequality

$$K \ll [PPh_3]$$

in which case eq 8 reduces to

$$k_{obsd} = k_1 + kK[ArI]/[PPh_3] \tag{9}$$

which is equivalent to expressions 2 and 3 in keeping with the experimental law derived from the straight line graph in Figure 2.

Kinetic evidence for predissociation of a phosphine ligand in reactions of type (I) is without precedent, and to the best of our knowledge only in one case,[16] the reaction of *trans*-$IrCl(CO)(PPh_3)_2$ with H_2, was the influence of added phosphine investigated. In this case no effect on the rate was observed. It should be noted, however, that the departure from "normal" first order observed for the reaction of *trans*-$IrCl(CO)(PPh_3)_2$ with benzyl chloride is typical of kinetic behavior indicative of predissociation of the reacting species.[17] A closer examination of this system may reveal behavior similar to that noted in our case. However, it is possible that the predissociation observed in our system is a result of the high temperature required for reaction with aryl iodides and that at lower temperatures predissociation is of negligible importance. As discussed below, predissociation permits now the rationalization of certain previously unexplained observations.[3,4]

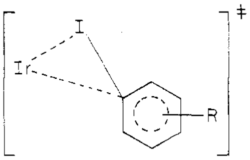
It should be noted that a three-coordinate intermediate, IrCl(CO)L, in place of the solvo-intermediate would yield indistinguishable kinetics. Although there is mounting evidence for such 14-electron species,[18] the fact that the stereochemistry with respect to the square plane of the starting material is maintained in the final product suggests that the coordination site vacated by the phosphine is occupied throughout the course of the reaction.

The two-term rate law (2) implies the operation of two parallel reaction paths both leading to the same final product, with the aryl halide not being involved in the activation step of the k_1 path. This behavior resembles the kinetics of substitution reactions[19] of square-planar d^8 complexes of Rh(I), Pd(II), Pt(II), and Au(III). The ligand-independent term of the typical two-term rate law

$$k_{obsd} = k_s + k_y[y]$$

(where s and y represent solvent and incoming ligand, respectively) represents a reaction path in which rate-determining solvolysis of the complex precedes rapid attack by the incoming group. To date the substitution kinetics of Ir(I) complexes have not been studied and it is not clear to what extent comparative behavior may be extrapolated from substitution in other square-planar systems. Two-term rate laws have not been observed for oxidative addition reactions, and if rapid, non-rate-determining addition to a solvolytic intermediate is involved, this (like the observation of phosphine predissociation) probably reflects the much higher temperatures used in this study. Obviously, other possible explanations exist for the k_1 path, and this subject requires more detailed study. All further discussion relates to the second-order path only.

Electronic Effects. Aryl Iodide. As can be seen in Figure 1, the presence of electron-attracting groups on the aryl ring increases the reaction rate. Only the methoxy-substituted aryl iodide deviates significantly from the positive Hammett correlation. Similar observations have previously been made for methoxyl reagents and apparently derive from the ability of the lone pairs on the methoxyl oxygen to interact with the metal atom.[20] From the positive value of the Hammett reaction coefficient, $\rho = +0.6$, certain preliminary conclusions can be drawn regarding the nature of the transition state. For organic reactions values of $|\rho| < |1|$ are generally indicative of essentially nonpolar transition states, while high values suggest major charge redistribution and separation in close proximity to the benzene ring. Linear transition states of type II are therefore unlikely. In three-center transition states of type I or III a positive ρ value could reflect stabilization of the negative charge on the iodine atom. However, since stabilization of a formal positive charge on the metal is also involved, the small experimental value of ρ probably reflects the net result of these mutually opposed requirements. The overall positive result thus probably suggests that stabilization of the negative charge is the dominant factor, leading to an asymmetrical three-center transition state in the sense



Comparison with early studies shows that the influence of electron-directing substituents on the addend AB is not well understood. Ugo et al.[4] found that the rates of reaction of para-substituted benzyl chlorides with *trans*-IrCl(CO)($PPh_{3-n}Et_n)_2$ did not follow the sequence expected on the basis of Hammett σ_p values. Different reactivity orders were observed for different values of *n*, but in general *p*-H- and *p*-$NO_2C_6H_4CH_2Cl$ reacted faster in benzene than their *p*-Cl and *p*-CH_3 analogues. This order was reversed for the reactions of *p*-bromobenzyl chloride although a contributory cause may have been the use of DMF as a solvent.[21]

Iridium Complex. Numerous studies[4,7,21,22] have related reactivity changes to the nature of the substituent on the phenyl ring(s) of PPh_3 in Vaska's compound. Linear free energy correlations using Hammett substituent constants have been found for the reaction of *trans*-IrCl(CO)[P(*p*-$ZC_6H_4)_3]_2$ with H_2, O_2, $C_6H_5CH_2Cl$, and CH_3I. The reaction constant, ρ, was negative in all cases, ranging from −0.7 for H_2 to −6.4 for MeI, indicating that enhanced electron density on the metal facilitated oxidative addition. Recently, Thompson and Sears[7] "discovered" the work of Kabachnik[14,15] on substituent constants for phosphorus compounds, $\sum\sigma^{ph}$, and showed that use of these values enabled better linear free energy correlations to be obtained for oxidative addition to Vaska-type complexes. All the reaction constants ρ^{ph} so obtained were still negative.

For the reactions of *m*-iodotoluene with a series of substituted derivatives of Vaska's compound, a good linear free energy relation was observed with the Kabachnik $\sum\sigma^{ph}$ values. However, the reaction constant differed from all previous studies in that positive, albeit small, values of ρ^{ph} were obtained. Previously accepted mechanistic ideas are incompatible with the apparent conclusion to be derived from these data, namely, that a decrease of the electron density on the metal atom enhances its ease of oxidation. Thus apparent contradiction can be explained in terms of the two-stage mechanism described by reactions 4–6. The predissociation stage is facilitated by less basic phosphines and would be reflected in a positive reaction constant ρ. On the other hand, in keeping with all the data accumulated to date, the oxidation rate is enhanced by increased electron density on the metal, i.e., a process characterized by a negative value for ρ. The net positive value observed is a measure of the relative importance of the two processes. It is significant that the two unique mechanistic features discovered for the reaction of IrCl(CO)($PAr_3)_2$ with aryl iodides, namely predissociation of PAr_3 and a positive value of ρ^{ph}, complement one another.

Both Ugo et al.[4] and Thompson and Sears[7] attribute the rate increase observed for complexes of more basic phosphines to inductive effects. It is therefore to be expected that the rate of reaction of $IrX(CO)L_2$ with various addends will increase as the basicity of the halide ligand X increases. However, for the reactions of IrX(CO)($PPh_3)_2$ with CH_3I, the rate order Cl > Br > I was observed, whereas for H_2 and O_2 the reactivity sequence is reversed.[3] Although a possible explanation may be related to the fact that the geometry of the addition for the homopolar molecules differs from that for CH_3I, it is difficult to rationalize this inversion of the reactivity sequence on electronic grounds.

Many studies have considered activation parameters in an attempt to categorize the mechanism of oxidative addition.[3–8,16,23] In the present system temperature dependence studies are of little value, but for the reaction of IrCl(CO)($PPh_3)_2$ with C_6H_5I, an activation energy of 123 kJ mol^{-1} was found. Activation enthalpies and entropies cannot be calculated because of the composite nature of K_{obsd}. Although in this regard we cannot compare the aryl iodide system to previously reported reactions, it is clear that the present kinetic study throws new light on the interpretation of oxidative addition reaction mechanisms.

Acknowledgment. We are grateful to the Israel Commission for Basic Research, The Israel Academy of Sciences and Humanities, for financial support of this study.

Registry No. *trans*-[IrCl(CO)($PPh_3)_2$], 15318-31-7; *trans*-[IrCl(CO)(P(*p*-$CH_3C_6H_4)_3)_2$], 28195-56-4; *trans*-[IrCl(CO)(P(*p*-$ClC_6H_4)_3)_2$], 34275-84-8; *trans*-[IrCl(CO)(P(*p*-$CH_3OC_6H_4)_3)_2$], 34054-03-0; C_6H_5I, 591-50-4; *p*-BrC_6H_4I, 589-87-7; *p*-ClC_6H_4I, 637-87-6; *p*-$CH_3C_6H_4I$, 624-31-7; *m*-$CH_3C_6H_4I$, 625-95-6; *p*-$CH_3OC_6H_4I$, 696-62-8.

Supplementary Material Available: Listings of pseudo-first-order rate constants (3 pages). Ordering information is given on any current masthead page.

References and Notes

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(2) Department of Organic Chemistry.
(3) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511 (1966).
(4) R. Ugo, A. Pasini, A. Fusi, and S. Cenini, *J. Am. Chem. Soc.*, **94**, 7364 (1972).
(5) M. Kubota, G. W. Kiefer, R. M. Ishikawa, and K. E. Bencala, *Inorg. Chim. Acta*, **7**, 195 (1973).
(6) J. Burgess, M. J. Hacker, and R. D. W. Kemmitt, *J. Organomet. Chem.*, **72**, 121 (1974).
(7) W. H. Thompson and C. T. Sears, *Inorg. Chem.*, **16**, 769 (1977).
(8) J. P. Collman and C. T. Sears, *Inorg. Chem.*, **7**, 27 (1968).
(9) J. Halpern and P. B. Chock, *Proc. Int. Conf. Coord. Chem., 10th*, 135 (1967).
(10) L. Vaska and L. Chen, *Chem. Commun.*, 1080 (1971).
(11) I. Douek and G. Wilkinson, *J. Chem. Soc. A*, 2604 (1969).
(12) J. Blum, M. Weitzberg, and R. J. Mureinik, *J. Organomet. Chem.*, **122**, 261 (1976).
(13) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **89**, 844 (1967).
(14) M. I. Kabachnik, *Dokl. Akad. Nauk SSSR*, **110**, 303, 393 (1956).
(15) T. A. Mastryukova and M. I. Kabachnik, *Russ. Chem. Rev. (Engl. Transl.)*, **38**, 795 (1969).
(16) H. Stieger and H. Kelm, *J. Phys. Chem.*, **77**, 290 (1973).
(17) R. G. Wilkins, "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes", Allen and Bacon, Boston, Mass., 1974.
(18) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972); R. Romeo, *Inorg. Chem.*, **17**, 2040 (1978).
(19) R. J. Mureinik, *Coord. Chem. Rev.*, **25**, 1 (1978), and references therein.
(20) See, e.g., W. H. Clement and I. Speidel, *Ind. Eng. Chem. Prod. Res. Develop.*, **9**, 220 (1970).
(21) J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Commun.*, 131 (1965).
(22) J. Halpern, *Acc. Chem. Res.*, **3**, 386 (1970).
(23) L. Vaska, *Inorg. Chim. Acta*, **5**, 295 (1971).