

A Kinetic Investigation of Some Electronic and Steric Factors in Oxidative Addition Reactions to Vaska's Compound

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Abstract: The kinetic parameters have been determined for the reactions of *trans*-IrCl(CO)(PEt_nPh_{3-n})₂ (*n* = 1, 2) and *trans*-IrCl(CO)[P(*p*-Z-C₆H₄)₂]₂ (Z = Cl, F, H, CH₃, OCH₃) with alkyl halides, hydrogen, and oxygen. Steric and electronic effects, established by substituent effects on the tertiary phosphine, are discussed. The reactivity and nature of the transition state in the case of different covalent molecules, such as alkyl halides, hydrogen, and oxygen, have been compared also in relation to the electronic properties of the covalent addendum.

Low-valent complexes of transition metals having mainly d⁸ and d¹⁰ electron configurations often add a covalent molecule to their coordination sphere as in the so-called oxidative addition reactions.¹ This general reaction has received a great deal of attention both from the point of view as an interesting new class of reactions of transition metal complexes and also as an important step in several homogeneous catalytic processes. Although the most important electronic features of this reaction have been discussed earlier by several authors,¹⁻⁴ little is known concerning secondary, but equally important, factors such as the effect of the basicity of the tertiary phosphine bound to the metal or ligand steric effects related to the bulkiness of the phosphorus substituents. Only very recently, when our paper was in preparation, Vaska and Chen have reported some studies where these latter effects were investigated.⁵ These secondary effects are not insignificant; indeed, in those reactions where tertiary phosphine complexes of transition metals are used as catalysts (for example, olefin hydrogenation,⁶ hydrogen extraction and transfer,⁷ hydroformylation,⁸ or olefin dimerization⁹) some dramatic changes can be obtained in catalytic activity or selectivity by introducing a phosphine ligand into the coordination sphere of the catalyst or by small changes of the steric and/or electronic properties of the substituents bound to the phosphorus atom. Interestingly, in these catalytic reactions there is always a step which can be considered as an oxidative addition reaction. It was thus of interest to ascertain what role is played by such a step in the overall catalytic process by studying how much it can be affected by electronic and also steric changes on the phosphorus atom.

Up to now the major emphasis on the effects of the tertiary phosphine has been given to electronic effects. Some recent investigations of Ni(0)¹⁰ and Pt(0)¹¹ tertiary

phosphine complexes have shown that steric effects can play a most important role in both the thermodynamic and kinetic stabilization of tetrahedral or trigonal complexes. It seems probable that steric effects are generally more important than previously supposed.

With the aim of commenting upon the relative importance of steric and electronic effects in phosphine complexes, we have carried out a kinetic investigation of oxidative additions to different *trans*-IrCl(CO)(PR₃)₂ complexes also comparing the behavior of rather different covalent molecules such as alkyl halides, hydrogen, and oxygen and studying in more detail the factors which define the interaction of the electronic density of the iridium atom with these covalent molecules.

In previous kinetic investigations of similar reactions of complexes of Ir(I)¹² and Rh(I),¹³ mechanistic data showed that the role of the covalent molecules is rather important in defining the rate of interaction. However, the real nature of the transition state obtained by adding different covalent molecules is unclear and a more extensive investigation is needed to ascertain the dependence of the rate on the properties of the addendum or on the properties of the iridium atom in the complexes.^{2,3}

Very recently some other investigations^{14,15} have confirmed earlier proposals¹² that the interaction of the iridium atom and the covalent molecule takes place in one step, although *cis* and *trans* addition are both possible in agreement with predictions made on the basis of orbital symmetry arguments. A kinetic investigation cannot provide decisive information on the energetics of the oxidative addition reaction² but as the transition state is certainly an activated one-to-one complex, with an overall resemblance to the reaction product,^{2,12,13} a comparative kinetic investigation, such as that reported here, may give some relative information about the energetics of the interaction of the covalent addendum with the low-valent metal complex and about the several factors affecting this interaction.

Experimental Section

Infrared and electronic spectra were recorded with a Perkin-Elmer 621 spectrophotometer and with a Beckman DK 2A spectrophotometer, respectively.

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Table I. Analyses and Relevant Spectroscopic Properties of Complexes of Formula *trans*-IrCl(CO)L₂

L	Calcd, %		Found, %		$\nu_{C=O}$, cm ⁻¹		ν_{Ir-Cl} , cm ⁻¹ Nujol	λ_{max} , nm benzene	10 ⁻³ ϵ
	C	H	C	H	Nujol	CH ₂ Cl ₂			
Ph ₃ P	56.9	3.8	56.5	3.9	1951	1960	317	387	3.89
Ph ₂ EtP	51.0	4.4	51.1	4.3	1943	1951	310	383	2.74
PhEt ₂ P	42.2	5.1	41.9	5.0	1936	1945	302	379	0.88
(<i>p</i> -ClC ₆ H ₄) ₃ P	44.9	2.4	44.8	2.6	1964	1966	320	389	1.55
(<i>p</i> -FC ₆ H ₄) ₃ P	49.9	2.7	49.3	2.8	1960	1964	321-327 (br)	385	0.43
(<i>p</i> -CH ₃ C ₆ H ₄) ₃ P	59.6	4.9	58.9	4.7	1944	1956	305-315 (br)	387	2.50
(<i>p</i> -CH ₃ OC ₆ H ₄) ₃ P	53.8	4.4	54.4	4.5	1954	1956	312	385	1.28

Tertiary phosphines were prepared *via* the classical method of reacting the corresponding phosphorus halide with the appropriate Grignard reagents (yield *ca.* 20-40%). All the alkyl halides were standard reagents but were redistilled or recrystallized before use; methyl iodide was extracted with an aqueous solution of thiosulfate, dried over molecular sieves, and distilled in a nitrogen atmosphere. Benzene was RS grade from C. Erba (Milan) and was distilled over sodium and deoxygenated with a stream of pure and dry nitrogen before use.

Preparation of the Iridium Complexes. All the complexes were obtained under a nitrogen atmosphere by adding a benzene solution of the appropriate tertiary phosphine to a benzene solution of IrCl(CO)₂(*p*-toluidine)¹⁶ (molar ratio of phosphine to iridium, 2.1 to 1). A loss of gas could be detected. When this was complete the yellow solution was gently heated for a few minutes; on cooling a yellow crystalline material precipitated.

With the diethylphenylphosphine complexes, addition of petroleum ether and low temperature ($\sim -5^\circ$) were required for precipitation. The compounds were filtered and recrystallized, under a nitrogen atmosphere, from toluene-petroleum ether or, as in the case of the diethylphenylphosphine complex, from petroleum ether by cooling the solution to -70° . Analytical and relevant spectroscopic data of the iridium compounds are reported in Table I.

Any attempt to prepare the triethylphosphine complexes through this route yielded an air-unstable yellow material whose ir spectrum possessed two carbonyl stretching frequencies of different intensity already reported¹⁷ for the analogous bromo complex. We ascribe this to the presence of a variable amount of the oxygen adduct, as indicated by the carbonyl absorption at higher wavelength and therefore the material was not used for further experiments.

Kinetic Experiments. The kinetics of the reactions of the complexes with alkyl halides were followed in dry benzene or other dry solvents by measuring (as already reported¹²) the rate of disappearance of the absorption band at around 380 nm (see Table I) in the presence of an excess of alkyl halide (*ca.* 100 times with respect to the iridium complex thereby providing pseudo-first-order conditions).

The kinetics of the reactions with hydrogen or oxygen were also followed by measuring the rate of disappearance of the absorption band at around 380 nm. Pseudo-first-order conditions were obtained by dissolving the complex at 10^{-4} - 10^{-6} M concentration in previously thermostated and gas-saturated benzene. A constant pressure of 1 atm of the gas was maintained over the solution in the cells (thermostated 5-cm cells were used in this case). The concentration of the gas in the solution was obtained from the reported solubility data;¹² it was always around 50-100 times higher than that of the iridium complex.

The value of our experimental method was tested by comparing the data obtained in the case of *trans*-IrCl(CO)(PPh₃)₂ with those reported by other authors¹² using different methods (see Table III or IV). The kinetic law,^{12,13} $-d[\text{complex}]/dt = k[\text{Ad}][\text{complex}]$, where [Ad] is the concentration of the covalent addendum, was always assumed. The results of all the kinetic measurements are reported in Tables II-V. The kinetic constants are average values of at least three experiments.

The standard deviation from the average values is usually negligible unless otherwise stated (see Tables II-V). In the case of *p*-fluoro- and *p*-chlorotriphenylphosphine complexes, the addition reaction of benzyl halides could be slightly affected by the reverse reaction corresponding to an equilibrium.^{2,13,15} We have deter-

Table II. Second-Order Rate Constants of the Reaction *trans*-IrCl(CO)[P(Et_nPh_{3-n})₂] + RX \longrightarrow IrCl(X)(R)(CO)[P(Et_nPh_{3-n})₂]

<i>n</i>	RX	<i>T</i> , °C	<i>k</i> , M ⁻¹ sec ⁻¹
0	CH ₃ I	25	$3.3 \pm 0.1 \times 10^{-3}$ ^{a,b}
0	C ₆ H ₅ CH ₂ Cl	25	$1.2 \pm 0.1 \times 10^{-4}$
0	C ₆ H ₅ CH ₂ Cl	40	1.5×10^{-4}
0	C ₆ H ₅ CH ₂ Cl	51	1.7×10^{-4}
0	C ₆ H ₅ CH ₂ Br	25	$1.0 \pm 0.1 \times 10^{-4}$
0	C ₆ H ₅ CH ₂ Br	40	$1.8 \pm 0.1 \times 10^{-4}$
0	C ₆ H ₅ CH ₂ Br	45	2.7×10^{-4}
0	C ₆ H ₅ CH ₂ Br	50	3.5×10^{-4}
1	CH ₃ I	25	$1.2 \pm 0.1 \times 10^{-3}$
1	CH ₃ I	30	$1.6 \pm 0.1 \times 10^{-2}$
1	CH ₃ I	35	1.9×10^{-2}
1	CH ₃ I	40	2.7×10^{-2}
1	C ₆ H ₅ CH ₂ Cl	25	$1.5 \pm 0.1 \times 10^{-3}$
1	C ₆ H ₅ CH ₂ Cl	35	$1.8 \pm 0.1 \times 10^{-3}$
1	C ₆ H ₅ CH ₂ Cl	40	$2.9 \pm 0.2 \times 10^{-3}$
1	C ₆ H ₅ CH ₂ Cl	45	$3.7 \pm 0.5 \times 10^{-3}$
1	C ₆ H ₅ CH ₂ Br	25	$1.2 \pm 0.05 \times 10^{-3}$
1	C ₆ H ₅ CH ₂ Br	30	2.6×10^{-3}
1	C ₆ H ₅ CH ₂ Br	35	3.2×10^{-3}
1	C ₆ H ₅ CH ₂ Br	40	5.1×10^{-3}
2	CH ₃ I	25	$1.4 \pm 0.1 \times 10^{-2}$
2	CH ₃ I	30	$2.0 \pm 0.1 \times 10^{-2}$
2	CH ₃ I	35	$2.4 \pm 0.1 \times 10^{-2}$
2	CH ₃ I	40	$3.0 \pm 0.1 \times 10^{-2}$
2	C ₆ H ₅ CH ₂ Cl	25	$5.5 \pm 0.4 \times 10^{-4}$
2	C ₆ H ₅ CH ₂ Cl	45	$5.1 \pm 0.4 \times 10^{-4}$
2	C ₆ H ₅ CH ₂ Br	25	1.3×10^{-4}
2	C ₆ H ₅ CH ₂ Br	35	3.5×10^{-4}
2	C ₆ H ₅ CH ₂ Br	40	5.6×10^{-4}

^a Reference 12 reported 3.5×10^{-3} . ^b *k* at 25° in other solvents: 7.6×10^{-3} (C₆H₅Cl); 1.0×10^{-2} (tetrahydrofuran); 2.1×10^{-2} (acetonitrile); 2.8×10^{-2} (dimethylformamide, in accordance with ref 12).

mined the equilibrium constants at 25° in the case of the addition of benzyl chloride to the *p*-chloro- and *p*-fluorotriphenylphosphine complexes (230 and 370 l. mol⁻¹, respectively). In both cases the equilibrium was proved by the appearance of isosbestic points at 466 and 460 nm, respectively. These values of the equilibrium constants are too high to think of any influence of the reverse reaction on the total rate when pseudo-first-order conditions are considered.

We have, however, observed that in the case of the above complexes the rate law of the reaction with benzyl chloride is not fully satisfied except in the first stages of the reaction (10% or more of conversion of the iridium complex). Kinetic constants have been obtained by easy extrapolation of the linear first-order plot corresponding to these first stages of the reaction. At higher conversion we observed a decrease of the rate of disappearance of the iridium complex which at the moment we are unable to rationalize. This trend was observed only in the case of reaction of benzyl chloride with *p*-chloro- and *p*-fluorotriphenylphosphine complexes.

Reaction products, which in many cases have already been studied and characterized, have not always been fully characterized. In some cases ir or nmr spectroscopy was used in order to ascertain the formation of Ir(III) species by oxidative addition; in the case of benzyl halides (used as solvents) a complex series of reactions has been reported to follow the addition reaction,¹⁸ which raises

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serious questions about whether the reactions of the benzyl chlorides are simple oxidative addition reactions.

By refluxing *trans*-IrCl(CO)(PPh₃)₂ and an excess of C₆H₅CH₂Cl in benzene under an inert atmosphere for 3 days, we have, however,

Table III. Second-Order Rate Constants of the Reaction *trans*-IrCl(CO)[P(*p*-Z-C₆H₄)₂]₂ + RX → IrCl(R)(X)(CO)[P(*p*-Z-C₆H₄)₂]₂^a

Z	RX	T, °C	k, M ⁻¹ sec ⁻¹
CH ₃	CH ₃ I	20	2.3 ± 0.1 × 10 ⁻²
CH ₃	CH ₃ I	25	3.3 ± 0.2 × 10 ⁻²
CH ₃	CH ₃ I	30	4.3 ± 0.1 × 10 ⁻²
CH ₃	C ₆ H ₅ CH ₂ Cl	20	2.5 ± 0.1 × 10 ⁻⁴
CH ₃	C ₆ H ₅ CH ₂ Cl	25	3.3 × 10 ⁻⁴
CH ₃	C ₆ H ₅ CH ₂ Cl	30	4.0 ± 0.2 × 10 ⁻⁴
CH ₃	C ₆ H ₅ CH ₂ Cl	40	4.9 × 10 ⁻⁴
CH ₃	CH ₃ I	20	1.6 ± 0.1 × 10 ⁻²
CH ₃	CH ₃ I	30	2.2 × 10 ⁻²
CH ₃	CH ₃ I	35	3.0 ± 0.4 × 10 ⁻²
CH ₃	C ₆ H ₅ CH ₂ Cl	25	1.2 ± 0.2 × 10 ⁻⁴
CH ₃	C ₆ H ₅ CH ₂ Cl	30	1.4 ± 0.1 × 10 ⁻⁴
CH ₃	C ₆ H ₅ CH ₂ Cl	40	1.7 ± 0.1 × 10 ⁻⁴
F	CH ₃ I	20	1.1 ± 0.1 × 10 ⁻⁴
F	CH ₃ I	25	1.5 ± 0.2 × 10 ⁻⁴
F	CH ₃ I	30	2.3 ± 0.2 × 10 ⁻⁴
F	C ₆ H ₅ CH ₂ Cl	25	1.5 ± 0.4 × 10 ⁻⁵
F	C ₆ H ₅ CH ₂ Cl	30	2.7 ± 0.3 × 10 ⁻⁵
F	C ₆ H ₅ CH ₂ Cl	40	3.6 × 10 ⁻⁵
Cl	CH ₃ I	25	3.7 ± 0.1 × 10 ⁻⁵
Cl	CH ₃ I	30	5.8 ± 0.5 × 10 ⁻⁵
Cl	CH ₃ I	35	7.8 ± 0.3 × 10 ⁻⁵
Cl	C ₆ H ₅ CH ₂ Cl	25	2.0 ± 0.5 × 10 ⁻⁵
Cl	C ₆ H ₅ CH ₂ Cl	30	2.6 ± 0.5 × 10 ⁻⁵
Cl	C ₆ H ₅ CH ₂ Cl	40	3.6 ± 0.7 × 10 ⁻⁵

^a Data for Z = H are reported in Table II.

Table IV. Second-Order Rate Constants of the Reaction *trans*-IrCl(CO)[P(*p*-Z-C₆H₄)₂]₂ + H₂ → IrH₂Cl(CO)[P(*p*-Z-C₆H₄)₂]₂

Z	T, °C	10k, M ⁻¹ sec ⁻¹
OCH ₃	20	4.8
OCH ₃	30	6.6
OCH ₃	40	9.3 ± 0.8
CH ₃	20	4.3
CH ₃	30	5.3
CH ₃	40	6.8
H ^a	20	5.0
H ^a	30	9.3
H ^a	35	13.0
F	20	1.7
F	30	2.5
F	40	6.2
Cl	20	1.7
Cl	30	2.6
Cl	40	5.0

^a These data are reported from ref 12.

obtained a completely different reaction trend. A white crystalline material separated slowly from the solution ($\nu_{\text{CO}} = 2050 \text{ cm}^{-1}$; $\nu_{\text{Ir-Cl}} = 303 \text{ cm}^{-1}$). This compound analyzed as the simple addition compound of the benzyl chloride to Vaska's compound (*Anal.* Calcd with 1 mol of benzene of crystallization: C, 60.8; H, 4.5. Found: C, 61.7; H, 4.4).

Increasing the reaction time and the excess of benzyl halides provided another white compound ($\nu_{\text{CO}} = 2078 \text{ cm}^{-1}$; $\nu_{\text{Ir-Cl}} = 322 \text{ (s), 315 (sh), 303 cm}^{-1} \text{ (w)}$) which analyzed as IrCl₃(CO)(PPh₃)₂.

It seems therefore that some side reaction follows the addition one. However, as benzyl halides were in great excess under our reaction conditions and as kinetics were followed by the disappearance of the Ir(I) complex, any subsequent reaction should not at all influence the measurement of the kinetics of the oxidative addition reaction, particularly when the rate of the reverse reaction is considered negligible.

Table V. Second-Order Rate Constants of the Reaction *trans*-IrCl(CO)[P(*p*-Z-C₆H₄)₂]₂ + O₂ → Ir(O₂)Cl(CO)[P(*p*-Z-C₆H₄)₂]₂

Z	T, °C	10 ³ k, M ⁻¹ sec ⁻¹
OCH ₃	20	7.4 ± 0.4
OCH ₃	25	10.0 ± 0.1
OCH ₃	30	11.1 ± 0.5
OCH ₃	35	14.0 ± 0.1
OCH ₃	40	15.9 ± 0.6
CH ₃	20	3.3 ± 0.2
CH ₃	30	5.2 ± 0.2
CH ₃	40	10.7 ± 0.7
H ^a	20	2.1
H ^a	30	3.9
H ^a	35	6.4
F	20	0.79 ± 0.05
F	30	1.31 ± 0.13
F	40	2.09 ± 0.12
Cl	20	0.51 ± 0.02
Cl	30	1.07 ± 0.01
Cl	40	1.67 ± 0.01

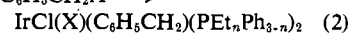
^a These data are reported from ref 12.

Results

The kinetic parameters of the reactions 1 and 2 with *trans*-IrCl(CO)(PEt_nPh_{3-n})₂ + CH₃I →



trans-IrCl(CO)(PEt_nPh_{3-n})₂ + C₆H₅CH₂X →



X = Cl, Br; n = 0, 1, 2

alkylphenylphosphine complexes were first determined. Under our experimental conditions (see Experimental Section) all the reactions went essentially to completion and followed second-order kinetics as already reported.^{2,12,13} Some selected values of second-order rate constants and of activation parameters are summarized in Tables VI and VII. Both reactions 1 and 2

Table VI. Second-Order Rate Constants at 25° and Activation Parameters of the Reaction *trans*-IrCl(CO)[PEt_nPh_{3-n}]₂ + CH₃I

n	k, M ⁻¹ sec ⁻¹	ΔH [‡] , kcal mol ⁻¹	ΔS [‡] , eu ^b
0	3.3 × 10 ⁻³	7.0	-47 ^a
1	1.2 × 10 ⁻²	9.8	-34
2	1.4 × 10 ⁻²	9.9	-34

^a Reference 12 reported 3.5 × 10⁻³ M⁻¹ sec⁻¹; 5.5 kcal mol⁻¹, and -51 eu. ^b At 25°.

Table VII. Second-Order Rate Constants at 25° and Activation Parameters of the Reaction *trans*-IrCl(CO)(PEt_nPh_{3-n})₂ + C₆H₅CH₂X

n	X	k, M ⁻¹ sec ⁻¹	ΔH [‡] , kcal mol ⁻¹	ΔS [‡] , eu ^a
0	Cl	1.2 × 10 ⁻⁴	4.6	-60
	Br	1.0 × 10 ⁻⁴	11.3	-39
1	Cl	1.5 × 10 ⁻³	8.8	-42
	Br	1.2 × 10 ⁻³	15.9	-20
2	Cl	5.5 × 10 ⁻⁴	<i>b</i>	<i>b</i>
	Br	1.3 × 10 ⁻⁴	18.3	-15

^a At 25°. ^b The activation energy of this reaction has been found to be ca. 0.

exhibited a constant behavior, the rate decreasing in the order PEtPh₂ ≥ PEt₂Ph > PPh₃. This behavior was unexpected as on the grounds of some previous in-

vestigations,^{1,4,5} it being anticipated that the reactivity of the iridium complexes should be enhanced by the presence of more basic phosphines (corresponding to an increase in the number of ethyl radicals bound to the phosphorus atom) which must increase the nucleophilicity of the iridium atom. Despite a net increase of reactivity going from the PPh₃ complex to the PEtPh₂ one, the PEt₂Ph complex shows a reactivity comparable to or even lower than that of the PEtPh₂ complex.

If the activation parameters are taken into consideration, it appears that the activation entropy has lower values in the case of ethyl-substituted phosphines. This fact suggests that some different steric effects in the transition state must be supposed and that the anomalous behavior could be related to these effects. The activation enthalpies have essentially constant values.

The markedly negative entropies of activation found here confirm that the transition state should be rather polar;¹² support for this view comes also from the fact that the activation entropy in reaction 2 is more negative with the more polar C-Cl bond than with the C-Br bond. In the formation of the transition state, a rather important factor may be the strength and polarity of the C-X bond of the alkyl halide since the positive charge on the carbon atom is attacked by a nucleophilic iridium atom.¹² However, in the reaction of different benzyl halides (Table VII) (reaction 2), there is only a small decrease of reactivity, with a corresponding increase in the activation enthalpy, when chlorine is substituted by bromine.

We therefore extended our investigations to include a study of the reaction of para-substituted benzyl chlorides with the series of complexes of type *trans*-IrCl(CO)(PEt_nPh_{3-n})₂ (Table VIII). The rate constants

Table VIII. Second-Order Rate Constants at 25° of the Reaction *trans*-IrCl(CO)(PEt_nPh_{3-n})₂ + *p*-Y-C₆H₄CH₂Cl

Y	<i>k</i> , M ⁻¹ sec ⁻¹		
	<i>n</i> = 0	<i>n</i> = 1	<i>n</i> = 2
H	1.2 × 10 ⁻⁴	1.5 × 10 ⁻³	5.5 × 10 ⁻⁴
F	7.2 × 10 ⁻⁵	9.5 × 10 ⁻⁵	1.2 × 10 ⁻⁴
Cl	6.4 × 10 ⁻⁵	1.0 × 10 ⁻⁴	1.4 × 10 ⁻⁴
CH ₃	3.7 × 10 ⁻⁵	7.0 × 10 ⁻⁵	2.0 × 10 ⁻⁴
NO ₂ ^a	~4.0 × 10 ⁻⁴	~10 ⁻³	~10 ⁻³

^a The constants when the addendum is *p*-NO₂-C₆H₄CH₂Cl were very imprecise and are to be considered only as indicative.

(25°) are seen to be much affected by the nature of the substituents in the para position. However (see Table VIII), the changes in reactivity (measured by log *k*₂₅) do not follow exactly the order of electron-withdrawing power, which could be inferred, for instance, from the Hammett constant σ_p of the para substituents.

The lack of any reasonably good linear correlation between log *k*₂₅ and σ_p of para substituents is rather common in the case of benzyl halides reactions.¹⁹ Our results with para-substituted benzyl chlorides are rather different from those reported by Halpern and Chock,²⁰ who have found that the rates with para-substituted benzyl bromides measured in dimethylformamide follow the order *p*-CH₃ > *p*-Br > *p*-H > *p*-NO₂ which is

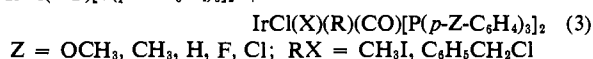
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opposite to what is reported here. However, this can be explained by the use of a different solvent such as dimethylformamide. In fact, dimethylformamide reacts with the alkyl halides;¹³ moreover in this solvent a very slow solvolysis of the Ir(I) complex may take place.²¹

Interestingly, it appears from the data reported in Table VIII that with some para-substituted benzyl chlorides (*p*-F and *p*-CH₃, for instance) the order of reactivity of the iridium complexes is IrCl(CO)(PEt₂Ph)₂ > IrCl(CO)(PEtPh₂)₂ > IrCl(CO)(PPh₃)₂ which corresponds to the order of basicity of the phosphorus atom.

In order to distinguish further between steric and electronic effects we have studied reaction 3 where the



reactivity of complexes having similar steric effects but rather different electronic structures is compared.

In Table IX the second-order rate constants at 25°

Table IX. Second-Order Rate Constants at 25° and Activation Parameters of the Reaction *trans*-IrCl(CO)(P(*p*-Z-C₆H₄)₃)₂ + RX → IrCl(R)(X)(CO)(P(*p*-Z-C₆H₄)₃)₂

Z	RX	<i>k</i> , M ⁻¹ sec ⁻¹	Δ <i>H</i> [‡] , kcal mol ⁻¹	Δ <i>S</i> _‡ , eu ^a
OCH ₃	CH ₃ I	3.5 × 10 ⁻²	8.8	-35
OCH ₃	C ₆ H ₅ CH ₂ Cl	3.3 × 10 ⁻⁴	5.9	-55
CH ₃	CH ₃ I	1.5 × 10 ⁻²	13.8	-20
CH ₃	C ₆ H ₅ CH ₂ Cl	1.2 × 10 ⁻⁴	8.6	-50
H	CH ₃ I ^b	3.3 × 10 ⁻³	7.0	-47
H	C ₆ H ₅ CH ₂ Cl ^c	1.2 × 10 ⁻⁴	4.6	-60
F	CH ₃ I	1.5 × 10 ⁻⁴	17.0	-20
F	C ₆ H ₅ CH ₂ Cl	1.5 × 10 ⁻⁵	11.4 ^d	-46 ^d
Cl	CH ₃ I	3.7 × 10 ⁻⁵	14.9	-28
Cl	C ₆ H ₅ CH ₂ Cl	2.0 × 10 ⁻⁵	7.2 ^d	-56 ^d

^a At 25°. ^b Data reported from Table VI. ^c Data reported from Table VII. ^d These data are obtained considering the main values reported in Table III; however, owing to the large errors of *k* values, they must be considered only as indicative.

and the activation parameters of reactions 3 are reported. Notable differences in rates are observed by changing the electronic properties of para substituents although they are connected to the iridium atom only indirectly through, for example, the π density on the phenyl rings of the phosphine ligand.

An increase of electronic density on the iridium atom, due to the effect of para substituents, increases the rate of interaction with the alkyl halide. This is due, as expected, to the increased nucleophilicity of the iridium atom which becomes a stronger base. By plotting log *k*₂₅ against the Hammett σ_p constants of the para substituents, two straight lines are obtained (Figure 1), showing that there is a direct relation between the basicity of the metal atom measured indirectly by σ_p and the overall kinetics. The different reactivity is certainly due in this case to electronic factors; indeed, while there are rather sensitive variations in the activation enthalpies, the activation entropies are sensibly constant (around 30 eu with CH₃I and around 50–60 eu with C₆H₅CH₂Cl) showing that steric factors remain nearly constant.

(21) R. Ugo and A. Pasini, unpublished observations.

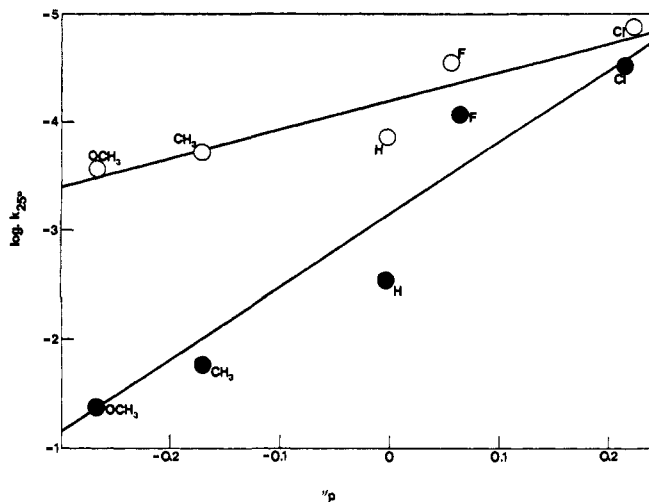


Figure 1. Plot of $\log k_{25}$ against σ_p for reaction 3 (\bullet = CH_3I , \circ = $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$).

If we consider Figure 1 and Table IX it is clear that the triphenylphosphine complex does not fit well into the general behavior of this series of complexes and with the other data of the series. This fact is not immediately explicable but it could be tentatively interpreted by a different solvation, in benzene, of the triphenylphosphine ligand, with respect to the para-substituted phosphine.

The results reported in Figure 1 and Table IX suggest thus that an evaluation is possible of the electronic factors underlying the kinetics of an oxidative addition reaction. Since the transition state is rather similar to the final product, we can compare, by a kinetic investigation, the nature of the interaction of the electronic density localized on the metal atom with any added covalent molecule. For this reason we have also investigated the interaction of two symmetrical covalent molecules, hydrogen and oxygen.

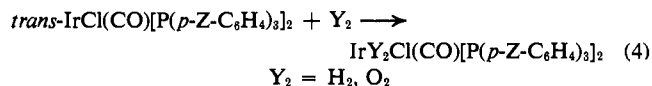
Table X lists the second-order rate constants at 25°

Table X. Second-Order Rate Constants at 25° and Activation Parameters of the Reaction $\text{trans-IrCl}(\text{CO})[\text{P}(p\text{-Z-C}_6\text{H}_4)_3]_2 + \text{Y}_2 \longrightarrow \text{IrClY}_2(\text{CO})[\text{P}(p\text{-Z-C}_6\text{H}_4)_3]_2$

Z	Y ₂	k, M ⁻¹ sec ⁻¹	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , eu ^a
OCH ₃	H ₂	5.6×10^{-1}	6.0	-39
OCH ₃	O ₂	10.0×10^{-2}	6.9	-40
CH ₃	H ₂	4.8×10^{-1}	4.3	-45
CH ₃	O ₂	4.3×10^{-2}	10.7	-29
H	H ₂ ^b	6.7×10^{-1}	10.8	-23
H	O ₂ ^b	3.4×10^{-2}	13.1	-21
F	H ₂	2.2×10^{-1}	11.6	-22
F	O ₂	1.3×10^{-2}	8.8	-38
Cl	H ₂	2.1×10^{-1}	9.8	-28
Cl	O ₂	7.2×10^{-3}	11.1	-31

^a At 25°. ^b Data from ref 12.

and the activation parameters of reaction 4. Interest-



ingly there is also with H₂ and O₂ an increased reactivity corresponding to an increasing basicity of the iridium

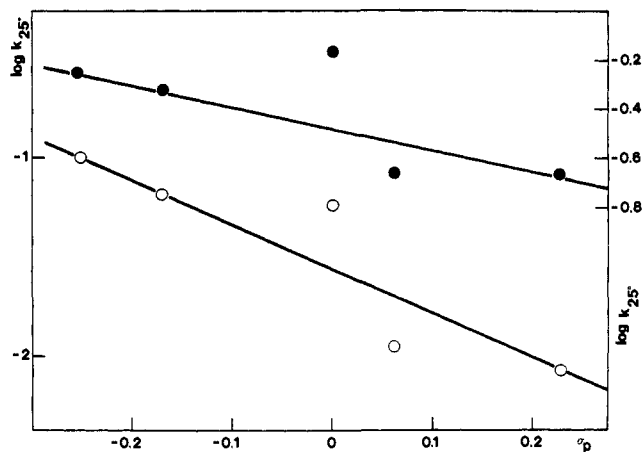


Figure 2. Plot of $\log k_{25}$ against σ_p for reaction 4 (\bullet = H₂, \circ = O₂).

atom; straight lines of different slopes are obtained by plotting $\log k_{25}$ against σ_p for both reactions (Figure 2). No great differences can be detected in the activation parameters of reactions with either hydrogen or oxygen (Table X); only with the *p*-tolylphosphine complex is there a relevant difference in the activation parameters. These data confirm that the interaction of the metal atom with hydrogen and oxygen is an acid-base interaction as suggested by Vaska,² in which the iridium atom acts as the basic center. If we also consider the data reported by Stromeier and co-workers²² and by Vaska,²³ the influence of steric effects with a small covalent molecule such as hydrogen are also manifest. In short, some steric effects could be related to the nature of the iridium complex irrespective of the covalent addendum.

Discussion and Conclusion

The results reported in this paper give some further insight into both the nature of the transition state of an oxidative addition of a covalent molecule to planar d⁸ complexes and the steric and electronic effects due to the phosphine ligands.

Up to now two slightly different types of transition-state geometries have been proposed for the oxidative addition reaction¹²⁻¹⁵ of alkyl halides. The addition of a heteropolar bond, such as the carbon-halogen bond, generally proceeds with a very large negative ΔS^\ddagger . This fact, in addition to the large dependence of the activation parameters on the solvent polarity and to the resemblance in the reactivity of substituted benzyl bromides toward both iridium complexes and tertiary amines, led some authors²⁰ to propose that oxidative addition of alkyl halides and consequently of other heteropolar bonds involved a highly linear polar transition state analogous to that proposed for the Menschutkin reaction of alkylation of tertiary nitrogen atoms.

Our work and other recent investigations have confirmed the large negative values of ΔS^\ddagger but some authors have not found a marked dependence of the rate on solvent polarity, as in the case of addition of silicon hydrides.¹⁵ We have, however, confirmed that the

(22) W. Stromeier and T. Onada, *Z. Naturforsch.*, **236**, 1527 (1968).

(23) L. Vaska and M. F. Werneke, *Trans. N. Y. Acad. Sci.*, **33**, 70 (1971).

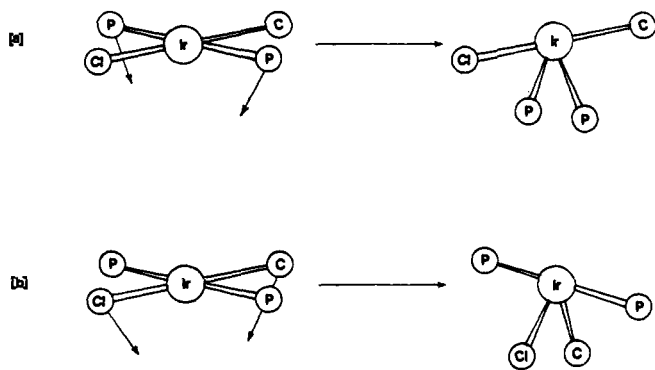


Figure 3. Bending of ligands to reach the transition state.

addition of methyl iodide to Vaska's compound shows a neat solvent effect when a large series of solvents with different polarities are considered (Table II). However, the increase of reactivity (measured by k_{25}) does not parallel closely the corresponding increase of solvent polarity.

In addition we have found a reaction behavior, in benzene, toward para-substituted benzyl halides which is rather different to that reported for the reaction of para-substituted benzyl halides toward pyridine (a case of a Menshutkin reaction).²⁴ It is possible therefore that a cyclic three-center transition state, already suggested to explain the reaction kinetic parameters of homopolar diatomic molecules with d^8 complexes,^{2,3} may also be applied for the analogous reaction with heteronuclear bonds.

As already pointed out by Harrod and Smith,¹⁵ the largely negative ΔS^\ddagger values can be in this case rationalized by an increased solvation due to the increased dipole in going from the ground state to the transition state. Such an increase in dipolar effects can be explained not only by a large dipolar interaction addendum-iridium atom (Menschutkin-type reaction mechanism) but also by a large deformation of the iridium complex from planarity to a pseudo-octahedral coordination (Figure 3) (three-center mechanism of cis addition).

A large increase of the dipole moment in the transition state would be obtained if the cis three-center addition takes place by bending the two trans phosphines into a cis arrangement (case a of Figure 3). This would accord with the appearance of steric effects mainly in the transition-state complex.

In the ground state there is generally a lack of steric effects; spectroscopic properties of $trans\text{-IrCl}(\text{CO})(\text{PR}_3)_2$ complexes such as ν_{CO} and $\nu_{\text{Ir-Cl}}$ show that there is a linear correlation (Figures 4 and 5) with $\Sigma\sigma^*$ in the case of ethylphenylphosphines (σ^* is the Taft constant) or σ_p in the case of para-substituted phenyl phosphines. Thus tertiary phosphines only exert an electronic effect in the precursor planar complexes and no steric effects are observed.

The mutual steric interaction of the two tertiary phosphine ligands in the transition state involves the interaction of a solid angle, corresponding to each tertiary phosphine, centered on the metal and just large enough to enclose the van der Waals radii of the outermost atoms of the ligand.¹⁰ When the two mutu-

(24) J. W. Baker, *J. Chem. Soc.*, 1448 (1936).

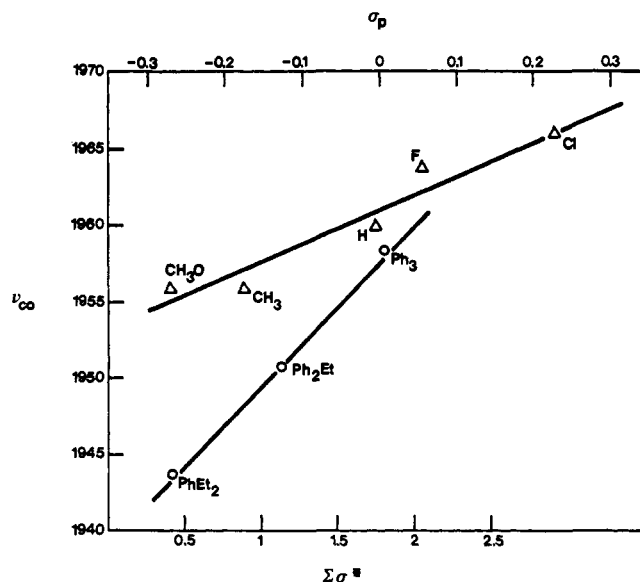


Figure 4. Plot of ν_{CO} against σ_p for $trans\text{-IrCl}(\text{CO})[\text{P}(p\text{-Z-C}_6\text{H}_4)_2]_2$ and against $\Sigma\sigma^*$ for $trans\text{-IrCl}(\text{CO})(\text{PEt}_n\text{Ph}_{3-n})_2$.

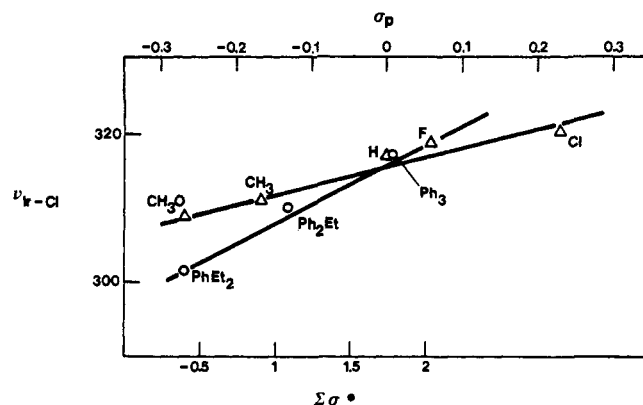


Figure 5. Plot of $\nu_{\text{Ir-Cl}}$ against σ_p for $trans\text{-IrCl}(\text{CO})[\text{P}(p\text{-Z-C}_6\text{H}_4)_2]_2$ and against $\Sigma\sigma^*$ for $trans\text{-IrCl}(\text{CO})(\text{PEt}_n\text{Ph}_{3-n})_2$.

ally trans tertiary phosphines bound to iridium move to a cis-octahedral arrangement the two cones begin to interact; the amount of interaction depends on the flexibility of the phosphorus substituents which fold back into as small a cone as possible.

In case b of Figure 3 such a steric effect should not be so evident. However, the reported studies on the geometry of the oxidative addition of alkyl halides to d^8 iridium complexes seem to be more in agreement with either a trans addition or an addition with a transition state corresponding to case b of Figure 3.²⁵

In the case of hydrogen or oxygen addition to $trans\text{-IrCl}(\text{CO})(\text{PPh}_3)_2$, the geometry of the final adduct corresponds to the transition-state geometry shown in Figure 3b² and again large steric effects, due to substituents on the phosphorus atom, have been independently pointed out by Stromeier²² and Vaska^{5,23} in their investigations of the kinetics and thermodynamics of the hydrogen and oxygen addition to $trans\text{-IrCl}(\text{CO})(\text{PR}_3)_2$ complexes (R = *n*-butyl, cyclohexyl, *m*-, *o*-, and *p*-tolyl, etc.).

(25) A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1128 (1969), and references cited therein.

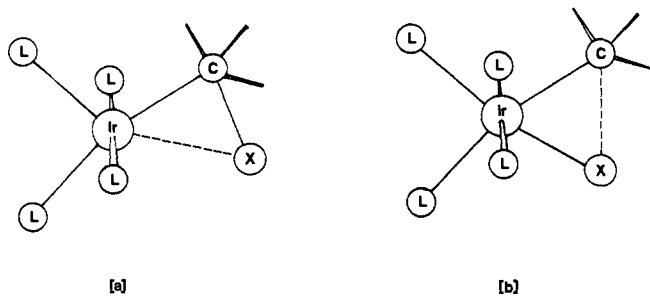


Figure 6. Models of transition-state geometry for reactions with alkyl halides.

Also a very recent report showed that the oxidative addition of alkyl halides to complexes of formula $C_5H_5M(CO)PR_3$ ($M = Co, Rh, Ir$) takes place with a Menschutkin-type reaction giving rise to an ionic reaction product. Despite that, large steric effects due to phosphines were detected²⁶ also. These facts are not consistent with a steric effect associated with the bending of the mutually trans phosphines. We have thus contrasting results which could be attributed to differences in the mechanistic details of the transition state on changing the bulkiness of the substituent on the phosphorus atom. Indeed it seems that this is an essentially "pure" spatial effect; some ligands (e.g., tricyclohexylphosphine) appear to completely isolate the metal center from the attacking hydrogen molecule without invoking a bending of the phosphine ligands.^{5, 23}

A recent paper by Graham and Davis²⁷ shows that a nearly ionic transition state as in the Menschutkin-type reaction does not agree with some of our experimental data. In fact, these workers, who have studied the addition of $C_6H_5CH_2X$ ($X = Cl, Br, I$) to $C_5H_5Rh(CO)PR_3$ (which takes place in a Menschutkin-type reaction), have found, as expected, a very large increase of reactivity in the following order, $I > Br \gg Cl$, while we did not find any great change of reactivity (Table VII).

We propose thus that the large ΔS^\ddagger and solvent effect could be explained by a rather polar, asymmetric three-center transition state such as in Figure 6a. In this case there is no simultaneous C-X bond breaking and Ir-X bond making (such as case b of Figure 6), but the iridium interaction takes place mainly on the carbon atom with a consequent lengthening of the carbon-halogen bond and formation of a weak iridium-halogen bond which is close to an ion pair.²⁶ Briefly the iridium attack does not proceed symmetrically into the heteropolar bond.

The transition state, although corresponding to a three-center mechanism, is not too far from that of a true Menschutkin-type reaction. In any case the Ir-C bond making appears to proceed to a greater extent than the carbon halogen bond breaking²⁸ as the reaction is favored both by strong electron-withdrawing substituents of the *p*-benzyl halides and by increasing the electronic density at the iridium atom.

However, the amount of carbon-halogen bond breaking and of iridium-halogen bond making in the transition state cannot be evaluated exactly at this time.

(26) A. J. H. Davis and W. A. G. Graham, *Inorg. Chem.*, **9**, 2658 (1970).

(27) A. J. H. Davis and W. A. G. Graham, *ibid.*, **10**, 1653 (1971).

(28) Reference 19, p 152.

Table XI. ρ Values for the Reaction
 $trans-IrCl(CO)[P(p-Z-C_6H_4)_3]_2 + XY \rightarrow$
 $IrClXY(CO)[P(p-Z-C_6H_4)_3]_2$

XY	ρ
CH_3I	-6.4
$C_6H_5CH_2Cl$	-2.6
O_2	-2.2
H_2	-0.7

The desirability of obtaining data on the addition of the related R_3SiH and R_3SiD species is evident.

Of course a concerted, three-center mechanism does not require an inversion at the carbon atom of the alkyl halides as reported by Pearson and Muir.¹⁴ However, some recent experimental evidence against this latter work²⁹ and the fact that inversion at the carbon atom can occur in a related reaction³⁰ add also some support to a simple SN_2 mechanism (Menschutkin-type reaction). In our picture of the transition state, where we propose a nonconcerted, rather polar three-center SN_2 attack, inversion or retention may both occur depending on the amount of Ir-halogen bond making in the transition state.

Finally it is interesting to compare the different reactivity of molecules such as alkyl halides, hydrogen, and oxygen. If we evaluate the slopes ρ of Figures 1 and 2 (taking into account a pseudo-Hammett equation $\log k_{25} = \rho\sigma_p + \beta$) we obtain the data reported in Table XI. Hydrogen is the covalent molecule which is less demanding from the electronic point of view in accordance with the recent conclusion reached by Vaska and Werneke²³ on the energy of the metal-hydrogen bonding. Moreover, it is well known that hydrogen activation by transition metal surfaces is a "facile" reaction by Boudart's definition³¹ and this characteristic seems also to be maintained in the case of reaction with transition metal complexes. With a "softer" molecule such as oxygen there is a much greater influence of the "softness" of the transition metal atom as expected on the ground of the large electronic transfer from the metal to oxygen.

The highly negative ρ values of the reaction with CH_3I agrees with the proposed models for the geometry of the transition state complex of the reaction with alkyl halides. First of all it shows that a large positive charge³² is formed into the iridium atom in the transition state, which is in agreement with a polar, asymmetric three-center geometry; moreover, the less negative ρ value found in the case of reaction with $C_6H_5CH_2Cl$ shows that the negative charge supplied from the iridium atom is easily dispersed into the benzene ring with a minor sensitivity of the electrophilic carbon atom to the electronic density into the iridium atom.

In conclusion, the electronic effects due to phosphine ligands are more important in those reactions in which a large localized charge transfer is formed in the transition-state complex.

Acknowledgments. We wish to thank Engelhard S.p.A. for a gift of $IrCl_3 \cdot 3H_2O$.

(29) G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **93**, 1529 (1971).

(30) J. A. Labinger, R. J. Brans, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970).

(31) M. Boudart, A. Aldag, J. E. Bensen, N. A. Dougharty, and C. G. Harkings, *J. Catal.*, **6**, 92 (1966).

(32) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, p 403.