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Mechanistic investigation of the oxidative addition reactions between different iridium (I) cyclooctadiene ([Ir(LL')(cod)]) complexes and iodomethane

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Abstract

The oxidative addition reactions between two different [Ir(cod)(LL')] complexes (LL' = hpt and AnMetha) and iodomethane was kinetically investigated. The rate of oxidative addition was determined as $2.2(2) \times 10^{-2}$ and $2.69(6) \times 10^{-2}$ M⁻¹ s⁻¹ for [Ir(cod)(hpt)] and [Ir(cod)(AnMetha)] in nitromethane respectively. The large negative entropy of activation for the above-mentioned reactions in different solvents clearly point to an associative mechanism. An intrinsic volume of activation of -30.5(3) and -28(3) cm³ mol⁻¹ was determined for [Ir(cod)(hpt)] and [Ir(cod)(AnMetha)], respectively. A linear transition state with large charge separation and central ion contraction due to oxidation, contributes to the negative volume of activation.

Keywords: Oxidative addition; Iridium; Cyclooctadiene; High pressure kinetics; Volume of activation

1. Introduction

Oxidative addition reactions of alkyl halides to square planar Ir(I) and Rh(I) complexes are of general importance in terms of the formation of metal alkyl complexes and their role/application in catalysed industrial and other processes. The use of [Ir(CO)Cl(PPh₃)₂] (Vaska) in the hydrogenation of alkenes as well as the polymerisation of styrene and the use of [Ir(cod)(*o*phen)Cl] in the conversion of methanol to acetic acid are two illustrative examples of the application of iridium (I) complexes in catalytic processes [1]. More than often oxidative addition forms part of these catalytic cycles and related mechanistic aspects are thus of prime concern.

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Detailed kinetic studies using a number of addend substrates like $Hg(CN)_2[2]$ and CH_3I [3] all have large negative entropies of activation indicative of the associative nature of these oxidative additions. A dispute which is often raised, especially for those reactions involving haloalkanes is whether these reactions take place *via* a free radical pathway or involve transition states of a concerted three-centered (I) or two-step S_N2 nature (II).



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The latter should produce an ionic intermediate (III) which is difficult to detect and is usually converted to the coordinatively saturated *cis*- or *trans*-oxidative addition product in a fast consecutive step. However, in the reaction of $[Pt(Me)_2(2,2'-Bipy)]$ [4] with CH₃I

in acetonitrile it was possible, using a low temperature ¹H NMR technique, to prove the existence of $[Pt(Me)_3(2,2'-Bipy)(NCCH_3)]^+I^-$ at -40 °C. It is thus evident that a polar as well as a good nucleophilic solvent may stabilise intermediates of this sort.

The effect of different solvents and elevated pressure was consequently also studied in order to obtain more information on the nature of the transition state. Results from the pressure-dependence kinetic study of the reaction between [Rh(Sacac)(CO)(PPh₃)] [5] (Sacac = thioacetylacetonato ligand) and CH_3I for example indicated an increase in reaction rate at higher pressure and solvent polarity [6], but both ΔS^{\neq} and ΔV^{\neq} varied slightly for the range of solvent polarities investigated. On the basis of the solvent independence of ΔV^{\neq} (-13.2(5)-18.3(9) cm³ mol⁻¹) it was concluded that this reaction proceeds via a concerted threecentred transition state (I) since a contradictory and significant solvent dependency would be expected for an ion-paired intermediate via a S_N2 process. The conclusion regarding a three-centred transition state for the latter reaction is however not a clear cut case since recent work indicated a more complicated rate constant, which following the oxidative addition also include a carbonyl insertion step. The reaction between $[Rh(cupf)(CO)(PPh_3)]$ [5] (cupf = cupferrate) and CH₃I indicated no correlation between the observed rate and the polarity (contrary to the above), but a large increase in V^{\neq} from -17.3(8) to -25.4(7) cm³ mol⁻¹ for non-polar to polar solvents, respectively, were observed. The authors postulated that these values are more in agreement with the formation of an ion-pair (II) intermediate which will be favoured by polar solvents. The oxidative addition of hydrogen and iodomethane onto the Vaska complex [7] resulted in the intrinsic volumes of activation, ΔV_{intr}^{\neq} , of -18 and $-17 \text{ cm}^3 \text{ mol}^{-1}$, respectively. These were considered to be consistent with the simultaneous formation of two Ir-H bonds for H₂ but only one bond for CH₃I corresponding to transition state (II). Volumes of activation, ΔV^{\neq} , of -31 and -44 cm³ mol⁻¹ for [Ir(cod) (phen)]⁺ and [Ir(cod)(phen)(I)] [8] were respectively found for the oxidative addition reactions with dioxygen in methanol. The larger negative value is ascribed to an additional contribution from the solvational component, ΔV_{solv}^{\neq} , due to the creation of ionic charges during end-on addition of O₂ to the more reactive and coordinatively saturated five-coordinate complex. Similarly, the oxidative addition rate of CH₃I onto [Ir(acac)- (cod)(Br)]⁻ [3] is faster compared to its four-coordinate precursor, [Ir(acac)(cod)] in line with an increased Lewis basicity for the five-coordinate complex [9].

We have in recent years investigated the oxidative addition reactions of $[Ir(\beta-diketone)(cod)]$ complexes $(\beta$ -diketone = 2,4-pentanedionato (acac) or 1,1,1-trifluoro-2,4-pentanedionato ligands (tfaa)) in different solvents, as well as the bromide catalysis of the oxidative addition reaction of CH₃I to [Ir(acac)(cod)] [3]. However, no detail solvent and pressure study was performed on any of these Ir(I) complexes. It was decided to synthesise new Ir(I)-cod complexes, containing different bidentate ligands, in order to determine the effect of the latter variation on the rate of oxidative addition reactions. In addition, we decided to perform a pressure and solvent study on these complexes to probe the transition state since the absence of any carbonyl ligand in these complexes eliminate the possibility of acyl formation and simplify the resulting kinetics.

2. Experimental

2.1. General considerations

Unless otherwise stated, all the chemicals used were of reagent grade, and all the preparations were carried out in air. The sodium salt of 1-hydroxy-2-pyridinethione (hpt) was obtained from Merck Chemicals. The NMR spectra were obtained at 293 K on a Bruker 300-MHz spectrometer.

2.2. Syntheses

2.2.1. N-methyl-4-methoxybenzothiohydroxamic acid

N-methyl-4-methoxybenzothiohydroxamic acid (An-Metha) ligand was prepared using the procedures previously described [10,11]. ¹H NMR results are reported in Table 1.

2.2.2. η^4 -Cycloocta-1, 5-diene(2-pyridinethiolato-Noxide- $\kappa O, \kappa S$) iridium (I), ([Ir(hpt)(cod)]) and η^4 -Cycloocta-1,5-diene(N-methyl-4-methoxybenzothiohydroxamato- $\kappa O, \kappa S$)-iridium (I), ([Ir(AnMetha)(cod)]) were prepared as follows:

About 0.45 mmol $[Ir(cod)Cl]_2$ in 15 cm³ DMF and 0.9 mmol LL' in 3 cm³ DMF was mixed and stirred for 2 min. The slow addition of water precipitated a yellow product. The centrifuged yellow precipitate was

Table 1 ¹H NMR data for different [Ir(LL')(cod)] complexes in CDCl₃

-			
Complex	Cod (ppm)	LL' (ppm)	CH ₃ (ppm)
AnMetha		δ 6.88, 7.37 (CH), δ 3.57 (CH ₃), δ 3.82 (OCH ₃), δ 10.88 (OH)	
[Ir(hpt)(cod)] [Ir(AnMetha)(cod)]	δ 1.70, 1.82, 2.20, 2.24 (CH ₂) δ 1.8, 2.25 (CH ₂), δ 3.96, 4.30 (CH)	δ 6.85, 7.25, 7.88, 8.34 (CH), δ 4.02, 4.28 (CH) 6.92, 7.27 (CH), δ 3.82(OCH ₃), δ 3.71 (CH ₃)	
$ [Ir(hpt)(cod)(CH_3)I]^a [Ir(AnMetha)(cod)(CH_3)I]^a $	δ 1.72, 1.83, 2.21, 2.24 (CH ₂), δ 4.04, 4.30 (CH) δ 1.81, 2.27 (CH ₂), δ 3.98, 4.31 (CH)	δ 6.85, 7.24, 7.88, 8.33 (CH) δ 6.93, 7.29 (CH), $δ$ 3.84(OCH ₃), $δ$ 3.72 (CH ₃)	δ 2.17 δ 2.20

^a Results obtained by subtracting the starting material spectra.

redissolved in warm acetone and precipitated by the slow addition of water. The bright yellow product was dried over P_2O_5 in a vacuum desiccator for ca. 15 h. Yield: 233 mg, 63% ([Ir(hpt)(cod)]) and 312 mg, 70% ([Ir(AnMetha)(cod)]). ¹H NMR results are reported in Table 1.

Both complexes were further characterised by means of X-ray structure determinations [12,13].

2.2.3. $(\eta^4$ -Cycloocta-1, 5-diene)iodomethyl(2pyridinethiolato-N-oxide- $\kappa O, \kappa S$) iridium (III), $([Ir(hpt)(cod)(CH_3)I])$ and $(\eta^4$ -Cycloocta-1,5diene)iodomethyl(N-methyl-4-methoxybenzothiohydroxamato- $\kappa O, \kappa S$) iridium (III), $([Ir(AnMetha)(cod)(CH_3)I])$ were prepared as follows:

About 0.2 mmol of the iridium complex and 6 mmol of CH_3I (30× excess) was dissolved in 10 cm³ acetone. The solution was heated after which it was left at room temperature to precipitate. ¹H NMR results are reported in Table 1.

Isolation of the product after the oxidative addition reaction yielded a mixture of the starting material as well as the product, confirming the existence of the equilibrium that exists between reactant and product and which is clearly illustrated by the different kinetic runs. The mixture of reactant and product existed even in the presence of a large excess of CH_3I . The NMR results for the product were obtained by subtracting or eliminating the reactant spectra.

2.3. Kinetics

All the solvents used during the kinetic study were purified and dried prior to its use. All the kinetic measurements at atmospheric pressure were performed on a GBC (model 916) double-beam UV/VIS spectrophotometer equipped with a thermostat cell holder (0.01 °C). The high-pressure kinetics was performed on a GBC (model 916) double-beam UV/VIS spectrophotometer equipped with a thermostat high-pressure cell. The oxidative addition reactions were followed at ca. 400 nm for acetone, 1,2-dichloroethane, chloroform and benzene and at 427 nm for nitromethane. The reaction between [Ir(LL')(cod)] and CH₃I in benzene were followed at lower pressure (between 1 and 110 MPa for all the other solvents) due to the crystallisation of benzene at pressures exceeding 90 MPa. Because all the plots of k_{obsd} vs. [CH₃I] gave non-zero intercepts, a complete concentration variation was performed at each pressure in order to obtain the correct volume of activation for the forward and reverse rate. All reactions were performed under pseudo-first-order conditions with CH₃I at least in tenfold excess. Typical experimental conditions were $[Ir] = 1.0 \times 10^{-3}$ M and $[CH_3I]$ varied between 1.0×10^{-2} and 0.5 M. The observed first-order rate constant were calculated from plots of $\ln(A_t \times A_\infty)$ versus time, where A_t and A_∞ are the absorbencies at time t and infinity, respectively. These plots were linear for at least 2–3 half-lives of the reaction. A non-linear least-squares program was used for the calculations.

2.4. Reaction volumes and q_p -values

A locally manufactured Carlsberg dilatometer [14] was used to determine the reaction volume for the reactions between [Ir(LL')(cod)] and CH₃I. The dilatometer which had a capillary with diameter = 0.5 mm was calibrated with double distilled water. The molar volume of water was calculated using ρ -values calculated at different temperatures (21–30 °C) [15].

The change in molar volume ($\Delta V_{\rm m}$) between two temperatures was calculated by difference.

The constants for this dilatometer were calculated from the straight line obtained from a plot of $\Delta V_{\rm m}$ vs. change in capillary height using a non-linear least squares program. Ethyleneglycol was used as solvent in the temperature bath that enabled better temperature control (±0.01 °C).

The $q_{\rm p}$ -values (25 °C) used in this study were obtained from a linear regression calculation using three values at different temperatures that were obtained from [16]. The calculated $q_{\rm p}$ -values (10^{-6} bar⁻¹) at 25 °C are as follows: nitromethane, 1.698; acetone, 5.647; 1,2-dichloroethane, 11.093; chloroform, 14.983; benzene, 16.263. The Kirkwood model [17], represented in Eq. (2), was used to determine the solvent influence on $\Delta V_{\rm solv}^{\neq}$:

$$\Delta V^{\neq} = \Delta V_{\text{intr}}^{\neq} + \Delta V_{\text{solv}}^{\neq} \tag{1}$$

$$=\Delta V_{\rm intr}^{\neq} - (N_0 \Delta u^2 / r^2) q_{\rm p}.$$
 (2)

3. Results and discussion

The oxidative addition reactions of the two different [Ir(cod)(LL')] complexes can be presented as follows:

$$[\operatorname{Ir}(\operatorname{cod})(\operatorname{LL}')] + \operatorname{CH}_{3}\operatorname{I} \underset{k_{-1}}{\overset{k_{1}}{\rightleftharpoons}} [\operatorname{Ir}(\operatorname{cod})(\operatorname{LL}')](\operatorname{CH}_{3})\operatorname{I}]$$
(3)

Under the selected conditions these reactions gave the expected second-order kinetics and the observed rate constant, k_{obsd} , depended linear on the iodomethane concentration, see Fig. 1, i.e.,

$$k_{\rm obsd} = k_1 [\rm CH_3 I] + k_{-1}.$$
 (4)

Solvents with a large variety of dielectric constants (ϵ) were used in this study in order to try and find some correlation between the volume of activation and the solvent properties. The values of k as a function of temperature, solvent and pressure are reported in Table 2.

The results in Table 2 clearly show that the rate of oxidative addition depends to a certain degree on the solvent in which it was performed. An increase of



Fig. 1. k_{obsd} versus [CH₃I] for the oxidative addition reaction of CH₃I with [Ir(hpt)(cod)] in acetone, $\lambda = 401$ nm.

approximately a factor 9 was observed for the oxidative addition reaction between [Ir(hpt)(cod)] and iodomethane as the solvents were changed from non-polar

Summary of the kinetic and activation parameters for the oxidative addition reactions between the [Ir(LL')(cod)] complexes and CH_3I at 25 °C with LL = hpt and AnMetha

Solvent ϵ $q_{\rm p} \times 10^6 (25 \text{ °C})$	Nitromethane 38.3 1.70	Acetone 20.7 5.65	1,2-Dichloroethane 10.4 11.09	Chloroform 4.9 14.98	Benzene 2.3 16.26						
						[Ir(hpt)(cod)]					
						$k_1 \times 10^2 (M^{-1} s^{-1})^a$	2.2(2)	0.7(2)	0.85(5)	0.66(3)	0.189(6)
$k_{-1} \times 10^3 (\mathrm{s}^{-1})^{\mathrm{a}}$	0.7(1)	0.47(2)	0.5(1)	1.42(3)	0.60(2)						
$K (=k_1/k_{-1}) (M^{-1})$	32(7)	$14.7(7)^{b}$	16(4)	4.7(3)	3.2(1)						
ΔH_1^{\neq} (kJ mol ⁻¹)	49(5)	53(4)	46(4)	53(1)	57(6)						
ΔS_1^{\neq} (J K ⁻¹ mol ⁻¹)	-111(16)	-109(5)	-131(13)	-110(4)	-107(19)						
$\Delta S_{-1}^{\neq} (J \text{ K}^{-1} \text{ mol}^{-1})$	5(39)	-50(7)	61(18)	-14.3(3)	_						
$\Delta V^{\neq}(k_1) \; (\mathrm{cm}^3 \; \mathrm{mol}^{-1})$	-30(3)	-26(3)	-22(2)	-20(2)	-18(1)						
$\Delta V^{\neq}(k_{-1}) \; (\mathrm{cm}^3 \; \mathrm{mol}^{-1})$	-79(20)	_	_	21(1)	_						
$\Delta \bar{V} (\mathrm{cm}^3 \mathrm{mol}^{-1})$	-74(7)	_	_	_	_						
$\Delta V_{intr}^{\neq} (cm^3 mol^{-1})$	-30.5(3)	_	_	_	-						
[Ir(AnMetha)(cod)]											
$k_1 \times 10^2 (M^{-1} s^{-1})^a$	2.7(6)	0.94(1)	1.10(1)	0.530(5)	0.553(1)						
$k_{-1} \times 10^3 \ (s^{-1})^a$	0.41(19)	0.97(4)	1.40(4)	2.24(2)	0.63(4)						
$K (=k_1/k_{-1}) (M^{-1})$	65(30)	$9.7(4)^{c}$	7.9(2)	2.37(3)	8.8(6)						
ΔH_1^{\neq} (kJ mol ⁻¹)	59(4)	40(2)	57(0.5)	59(4)	59(1)						
ΔH_{-1}^{\neq} (kJ mol ⁻¹)	_	64(4)	86(7)	89(4)	78(2.5)						
ΔS_1^{\neq} (J K ⁻¹ mol ⁻¹)	-76(13)	-152(8)	-92(2)	-91(13)	-96(4)						
$\Delta S_{-1}^{\neq} (J K^{-1} mol^{-1})$	_	-89(12)	-10(23)	0.82(3)	-44(8)						
$\Delta V^{\neq}(k_1) \; (\mathrm{cm}^3 \mathrm{mol}^{-1})$	-28(3)	_	_	_	_						
$\Delta \bar{V} (\mathrm{cm}^3 \mathrm{mol}^{-1})$	-68(6)	_	_	_	_						

^a Subscript 1 refer to forward reaction (k_1) and -1 to reverse reaction (k_{-1}) .

^b K = 9(1) M⁻¹ spectrophotometric.

^c K = 23(3) M⁻¹ spectrophotometric.

Table 2

(benzene) to polar solvents (nitromethane) (see Fig. 2). An increase of only a factor 4 were observed for the corresponding reaction between [Ir(AnMetha)(cod)] and iodomethane. These results suggests that charge separation in the transition state is better assisted by the polar solvents, i.e., linear transition state. This increase in the forward rate constant, k_1 , is relative small compared to the increase which was observed for the same reaction between [Rh(Sacac)(CO)(PPh₃)] and iodomethane [6]. A 20-fold increase was observed for this reaction when it was performed in more polar solvents. The summary of kinetic results for different Ir(I) complexes listed in Table 3 show some important tendencies. The rate constants cited are the ones that were done in the most polar solvents. The following tendency was observed for the different bidentate ligands [9]:

macsm > AnMetha > hpt > Sacac > tfaa > cupf

This tendency is attributed to the electron donor ability of the "bite atoms" of the bidentate ligands bonded to the metal ion. These "bite atoms" increase the electron density on the metal ion, i.e., increase in the Lewis basicity, and thereby increase the rate of oxidative addition for these complexes. The large negative entropy of activation obtained for the reactions of both Ir(I) complexes in all the different solvents is indicative of an associative mechanism.

Large negative volumes of activation were obtained for these reactions in the different solvents that are also indicative that these reactions occur via an associative mechanism. A steady increase in the volume of activation from non-polar to polar solvents was observed. The plot of volume of activation vs. the calculated q_p (effect of pressure on the dielectric constant) values is presented in Fig. 3 which clearly indicates a linear relationship between the volume of activation and the solvent polarity. The straight line according to Eq. (2) has an intercept which represents the intrinsic volume of activation for the reaction. The results in Fig. 3 clearly indicates that the same transition state exists within all the solvents used in this study and that the reaction between [Ir(hpt)(cod)] and CH₃I has an intrinsic volume of activation of -30.5(3) cm³ mol⁻¹.

Predictions about the transition state of these reactions can be made by using the intrinsic volume of activation value of -30.5 cm³ mol⁻¹ for [Ir(hpt)(cod)] and



Fig. 2. k_{obsd} versus [CH₃I] for the oxidative addition reaction of CH₃I with [Ir(hpt)(cod)] in acetone, benzene and nitromethane.



Fig. 3. The volume of activation versus the calculated q_p for the oxidative addition reaction of CH₃I with [Ir(hpt)(cod)] at 25 °C in the different solvents.

Table 3

Summary of the second-order rate constants for the oxidative addition reactions of different [Ir(LL')(cod)] complexes with CH₃I

Donor atom	Ring size	$(10^3) k_1 (M^{-1} s^{-1})$	Solvent	Ref.
S–N	6	28.4(7)	acetonitrile	[9]
S–O	5	26.9(6)	nitromethane	this study
S-O	5	22(2)	nitromethane	this study
S-O	6	5.2(3)	acetonitrile	[9]
0–0	6	4.4(2)	acetonitrile	[9]
0–0	6	2.17(7)	acetonitrile	[9]
	Donor atom S–N S–O S–O S–O S–O O–O O–O	Donor atom Ring size S-N 6 S-O 5 S-O 5 S-O 6 O-O 6 O-O 6 O-O 6	Donor atomRing size $(10^3) k_1 (M^{-1} s^{-1})$ S-N628.4(7)S-O526.9(6)S-O522(2)S-O65.2(3)O-O64.4(2)O-O62.17(7)	Donor atom Ring size $(10^3) k_1 (M^{-1} s^{-1})$ Solvent S-N 6 28.4(7) acetonitrile S-O 5 26.9(6) nitromethane S-O 5 22(2) nitromethane S-O 6 5.2(3) acetonitrile O-O 6 4.4(2) acetonitrile O-O 6 2.17(7) acetonitrile

-28(2) cm³ mol⁻¹ for [Ir(AnMetha)(cod)]. The results in Table 2 show the solvation component of the volume of activation for the different solvents. For the reaction in benzene, a positive value of +12.5 cm³ mol⁻¹ is needed to give an overall volume of activation of -18 cm³ mol⁻¹. This solvation effect is probably due to the decrease in non-polar solvent interaction with a highly polar trigonal bipyramidal transition state with its large charge separation during the formation of the transition state, i.e., linear transition state.

The reaction volume $(\Delta \bar{V})$ for the reaction between [Ir(hpt)(cod)] and iodomethane was determined as -74(7) cm³ mol⁻¹. Due to the large experimental error on the volume of activation for the reverse reaction $(\Delta V^{\neq} = -79(20) \text{ cm}^3 \text{ mol}^{-1})$ no useful deduction could be made from these values. Using the reaction volume as well as the volume of activation and Eq. (5) the activation volume for the reverse reaction could be calculated [18]:

$$\Delta V = \Delta V_{\text{forward}}^{\neq} - \Delta V_{\text{reverse}}^{\neq},$$

$$\Delta V_{\text{reverse}}^{\neq} = +44 \text{ cm}^3 \text{ mol}^{-1}.$$
(5)

The corresponding value for [Ir(AnMetha)(cod)] is calculated as +40 cm³ mol⁻¹. The volume profile for the reaction between [Ir(hpt)(cod)] and CH₃I is given in Fig. 4, indicating the slightly asymmetric nature of the intrinsic and solvational reorganisation in the transition state.

A possible explanation for the negative intrinsic volume of activation for both complexes can be attributed to both electronic and bonding factors present in the transition state. The combined effect of the nuclear contraction due to the oxidation of Ir(I) to Ir(III) during the reaction as well as the new bond formation between the iridium centre and the methyl group of CH₃I adequately explains the magnitude of the negative intrinsic volume of activation for the forward reaction. The crystal structures of both [Ir(acac)(cod)(CH₃)I] [19] and [Ir(Sacac)



Fig. 4. Volume profile for the reaction of [Ir(hpt)(cod)] with CH₃I.

(cod)(CH₃)I] [20] clearly indicated the trans orientation of the methyl and iodide in the structures. The I-Ir-CH₃ angle of 156° in both structures was within experimental error the same and deviated significantly from the expected 180°. This large deviation is attributed to repulsion between the two trans ligands and the four protons bonded to the four ethylene carbons of the cod ligand. This repulsion between the cod and the incoming CH₃I as well as the relative inflexible geometry of the four coordinated complex ([Ir(hpt)(cod)]), make a three centre transition state between CH₃I and Ir in the transition state highly unlikely. The more favourable transition state is therefor the linear S_N2 transition state. The S_N2 intrinsic mechanism is also more favoured for oxidative addition reactions as indicated by ab initio calculations performed by Griffin et al. [21] for the reactions between $[M(CO)_2I_2]^-$ (M = Rh, Ir) and CH₃I. The relative large positive value for the volume of activation (+44 cm³ mol⁻¹) of the reverse reaction (k_{-1}) are explained in terms of the breaking of two bonds (Ir-I and Ir-CH₃) as well as the volume increase due to the reduction of the Ir(III) to Ir(I) for the reverse reaction (reductive elimination) which takes place via a dissociative mechanism.

A linear relationship between the volume of activation and q_p values was also observed by Steiger and Kelm for the oxidative addition reaction between [Ir(-CO)(Cl)(PPh₃)₂] and CH₃I [7]. A much smaller intrinsic volume of activation, $\Delta V^{\neq} = -17 \text{ cm}^3 \text{ mol}^{-1}$, was obtained for this reaction. It is interesting to note that the contribution of the solvolysis component to the volume of activation was also the largest for the non-polar solvents. In this case, contrary to our study, they observed an increase in negative activation volume for the non-polar solvents which they attributed to the formation of a linear transition state. A volume of activation of $-44 \text{ cm}^3 \text{ mol}^{-1}$ was obtained for the *cis* addition of O_2 to the $[Ir(phen)(cod)]^+$ [8] and it is well known that this reaction takes place via a concerted three-centre mechanism.

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