Bromide Catalysis in the Oxidative Addition of Iodomethane to Iridium(I) Complexes

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Abstract

[Ir(cod)(β-dik)] complexes (β-dik = 2,4-pentane-dionato or 1,1,1-trifluoro-2,4-pentanedionato ligands; cod = cycloocta-1,5-diene) react with CH_3I in acetone to form Ir(III) alkyl compounds. The addition of Br^- led to the formation of a five-coordinate inter-mediate which enhanced the reaction rate of the acac complex and gave the same oxidative addition product compared to the uncatalysed reaction. A reaction mechanism is given.

Introduction

The oxidative addition of CH_3I to square-planar d^8 complexes is important from an industrial view-point, especially for its well-known role in the Monsanto process for acetic acid [1]. One of the factors affecting the reactivity of these complexes towards CH_3I is the inherent Lewis base character of the usual low-valent, electron-rich metal catalyst. It is thus not surprising that cationic types like $[Ir(cod)L_2]^+$ (L = phosphine), described as Lewis acids, do not react with CH_3I but do add H_2 and HCl [2]. Similar behaviour also applies in the HCl addition to neutral complexes such as [Ir(cod)(Cl)-($PEtPh_2$)] [3]. In these two cases the metal center is activated towards oxidative addition by first forming a more electron-rich five-coordinate complex via halide ion addition. The greater reactivity of five-coordinate iridium(I) complexes, compared to their square-planar precursors, was further illustrated by iodide catalysis in the oxidative addition of CH_3I to [Ir(cod)(phen)]X (X = Cl^-, I^-) [4] (Scheme 1).
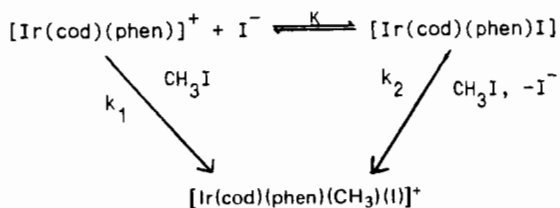
Scheme 1.

During our research on oxidative addition reactions of Rh(I) complexes it was found that [Rh-(acac)(cod)] does not react with CH_3I but that its more reactive iridium analogue does at a measurable slow rate. This prompted us to investigate the mechanism of this oxidative addition reaction and to observe whether bromide catalysis would follow the same pattern observed for the other halide ions.

Experimental

[Ir(cod)(β-dik)] complexes were prepared by addition of a tenfold molar excess of the β-diketone to a dimethyl formamide solution of the dimer [Ir(Cl)-(cod)]$_2$ (Strem Chemicals), precipitating the complex by addition of water followed by recrystallization from acetone through vacuum distillation at room temperature. In the case of the acac complex the DMF solution was warmed to *c.* 60 °C for a few minutes to ensure complete reaction. ^1H NMR spectra (Bruker AM 300, chemical shifts relative to TMS, δ = 0.0) were recorded in C_6D_6 at 296 K.

[Ir(acac)(cod)], yellow crystals: δ 5.1 (s, 1H, CH), 4.3 (m, 4H, CH), 2.2 (m, 4H, CH_2), 1.7 (d, 6H, CH_3), 1.5 (m, 4H, CH_2).

[Ir(tfaa)(cod)], yellow–orange crystals: δ 5.55 (s, 1H, CH), 4.27 (m, 4H, CH), 2.08 (m, 4H, CH_2), 1.48 (m, 4H, CH_2), 1.38 (s, 3H, CH_3).

[Ir(hfaa)(cod)] (hfaa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione), red–brown crystals: δ 6.0 (s, 1H, CH), 4.2 (m, 4H, CH), 1.95 (m, 4H, CH_2), 1.35 (m, 4H, CH_2).

[Ir(acac)(cod)(CH_3)(I)] was prepared by adding a tenfold molar excess CH_3I to an acetone solution of [Ir(acac)(cod)], vacuum distillation of the solvent and recrystallization from a petroleum ether (boiling point 80–100 °C) solution. This yellow compound was fully characterized by a crystal structure deter-mination [5].

Kinetic measurements for the uncatalysed oxid-ative addition reactions were made at 375 nm. The absorbance measurements for the formation of the five-coordinate complex as well as those for the subsequent oxidative addition were done at 404 nm. Kinetic data were collected under pseudo first-order

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conditions using a typical complex concentration of 3×10^{-4} M and iodomethane varying between 5×10^{-3} and 1.5 M. Good pseudo first-order plots of $\ln(A_t - A_\infty)$ versus time prevailed throughout and all data were subjected to the appropriate equation using a non-linear least-squares program [6]. Redistilled acetone was used as solvent. Iodomethane (Merck) was checked by ^{1}H NMR spectroscopy and used without further purification. A Hitachi model 150-20 spectrophotometer equipped with a thermostated cell (0.1 K) was used for all measurements.

Results and Discussion

The three β-diketone complexes prepared for this study are expected to show increasing Lewis basicity and have oxidative addition rates [7] in the order of hfaa < tfaa < acac in line with similar trends for the pK_a values of these ligands. Preliminary tests on [Ir(acac)(cod)] with regard to solution stability showed reaction with acetone, ethyl acetate, toluene, methanol and acetonitrile. The latter two gave relatively fast reactions whilst the decomposition in acetone proved suitable for the duration of the kinetic experiments. On the other hand [Ir(hfaa)-(cod)], being the least reactive towards CH$_3$I, decomposed faster in acetone compared to the oxidative addition rate and we thus dropped any further work on this complex.

The oxidative addition of CH$_3$I to the acac and tfaa complexes gave the expected second-order kinetics, i.e.

$$\text{Rate} = k_1[\text{CH}_3\text{I}][\text{Ir}(\beta\text{-dik})(\text{cod})] \qquad (1)$$

The second-order rate constants (k_1) and activation parameters are given in Table 1. The rate for the acac complex, being the stronger Lewis base of the two, exceeds that of the tfaa complex by a factor c. 13. The large negative entropies of activation suggest a highly polar transition state or marked increase in stereochemical restrictions in going from reactants to the activated state. The crystal structure determination of [Ir(acac)(cod)(CH$_3$)(I)] showed that CH$_3$ and I are bonded in a *trans* fashion which suggest that a S_N2 ionic mechanism [8] involving some degree of ionization in the transition state, i.e. [Ir(acac)-(cod)(CH$_3$)]$^+$I$^-$, may be operative. Depending on the reactivity of the system, transition states similar to the latter may become detectable intermediates at low reaction temperatures [9].

The addition of LiBr to [Ir(acac)(cod)] resulted in the different spectral changes depicted in Fig. 1 of which the isosbestic points at 397 and 422 nm are indicative of only one complex formed in this reaction. In the determination of this equilibrium constant the LiBr concentration was varied between 1.04×10^{-4} to 1.04×10^{-2} M, solutions for which

TABLE 1. Kinetic and equilibrium data for acac and tfaa complexes at 25 °C in acetone

	tfaa	acac
$10^3 k_1$ (M^{-1} s^{-1})	1.33(3)	16.9(2)
$\Delta H^*(k_1)$ (kJ mol^{-1})	40(3)[a]	36(2)[b]
$\Delta S^*(k_1)$ (J K^{-1} mol^{-1})	−165(10)[a]	−157(6)[b]
$10^{-3} \times K_2$ (M^{-1})		2.00(25)
k_3 (M^{-1} s^{-1})		2.57(5)
$10^3 \times k_4$ (s^{-1})		8.3(7)
k_6 (s^{-1})		0.18(11)
K_5		0.38(29)

[a]Determined from data at three temperatures. [b]Determined from data at six temperatures.
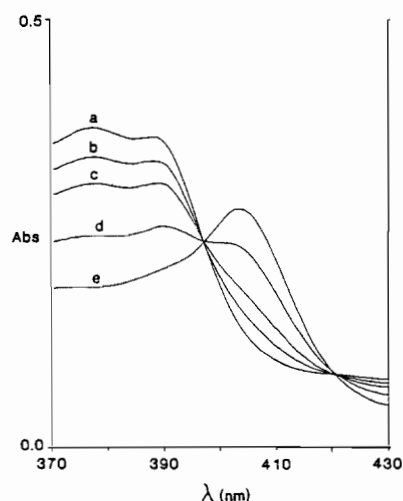
Fig. 1. Spectral changes observed upon addition of LiBr to 3×10^{-4} M [Ir(acac)(cod)] (a) in acetone: (b) 2×10^{-4}; (c) 3.98×10^{-4}; (d) 7.97×10^{-4}; (e) 3.98×10^{-3} M LiBr.
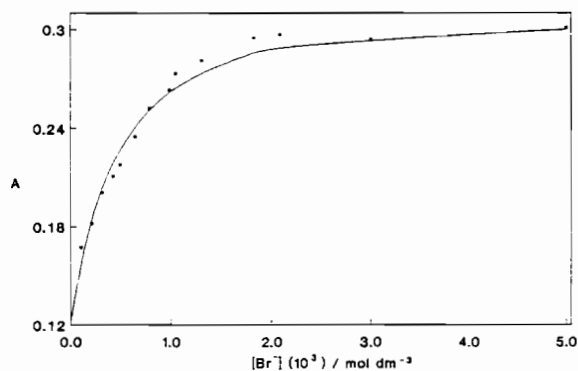

Fig. 2. Plot of absorbance vs. [LiBr] at 25 °C in acetone, $\lambda = 404$ nm.

the absorbance changes are depicted in Fig. 2 when measured at the peak maximum of 404 nm. From the definition of K_2 (see Scheme 2), Beer's law and mass balance, eqn. (2) can be derived.

$$A = (A_M + A_{ML}K_2[\text{Br}^-])/(1 + K_2[\text{Br}^-]) \qquad (2)$$

A is the absorbance at a given concentration LiBr, A_M and A_{ML} are the absorbances of [Ir(acac)(cod)] and [Ir(acac)(cod)(Br)]$^-$, respectively. The absorbance versus [LiBr] data were fitted to eqn. (2) to obtain the value of K_2 (Table 1). This value is larger by a factor ten if compared with 227 M^{-1} for the reaction between [Ir(phen)(cod)]$^+$ and I$^-$ [4]. Our K_2 value should however be considered as a composite equilibrium constant. LiBr is known to be a weak electrolyte [10] in acetone according to the equilibrium

$$\text{LiBr} \rightleftharpoons \text{Li}^+ + \text{Br}^-; \qquad K_1 = 5.22 \times 10^{-4}$$
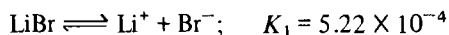
so that K_2 (actual) $= K_2/K_1 = 3.8 \times 10^6$ M^{-1}.

As a result of the large formation constant of [Ir(acac)(cod)(Br)]$^-$, the kinetic measurements for the bromide-catalysed pathway were all done in 8×10^{-3} M LiBr solutions thus ensuring no complications due to unreacted [Ir(acac)(cod)]. We also tried to measure the forward rate of the K_2 equilibrium but the reaction was too fast to detect by the stopped-flow technique.

The absorbance–time data plot for bromide catalysis and [CH$_3$I] = 0.05 M is biphasic which comprises an absorbance decrease for the faster reaction followed by an increase for the slower one. It was thus possible to study the faster reaction in the range $0.005 < $ [CH$_3$I] < 0.05 M and the slower one in the range $0.05 < $ [CH$_3$I] < 0.9 M. The faster reaction gave second-order kinetics according to eqn. (3).

$$\text{Rate} = k_3[\text{CH}_3\text{I}][\text{Ir(acac)(cod)(Br)}^-] \qquad (3)$$

The ratio $k_3/k_1 = 152$ is quite large if compared with $k_2/k_1 \sim 7$ for Scheme 1 and shows that bromide catalysis is much more efficient for the present system.

Plots of the pseudo first-order rate constants, k_{obs}, against varying [CH$_3$I] gave a curve which extrapolated to a non-zero intercept for the slower reaction. Subtracting this intercept value (at [CH$_3$I] = 0.0) from each of the k_{obs} values in the set and plotting the reciprocals $(1/k'_{obs})$ against $1/$[CH$_3$I] gave a straight line with intercept $1/k_6$ and slope = $1/K_5k_6$. This behaviour conforms to eqn. (4).

$$k_{obs} = k_4 + \frac{k_6K_5[\text{CH}_3\text{I}]}{1 + K_5[\text{CH}_3\text{I}]} \qquad (4)$$

The k_4, K_5 and k_6 values (Table 1) were calculated by fitting the k_{obs} versus [CH$_3$I] data to eqn. (4). According to these experimental results (fast and slow reaction), Scheme 2 may be proposed.

Since the bromide-catalysed pathway involved LiBr and CH$_3$I we also checked the reaction rate of the Finkelstein substitution

$$\text{LiBr} + \text{CH}_3\text{I} \longrightarrow \text{LiI} + \text{CH}_3\text{Br}$$

Scheme 2.
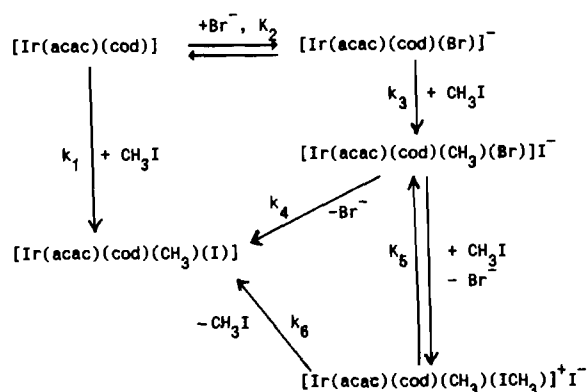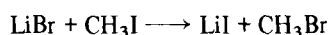
reported some years ago [10]. At [CH$_3$I] = 0.99 M (a maximum concentration employed in our study) and [LiBr] = 0.008 M this reaction proceeds with $t_{1/2} = 20.7$ min which is well above the total reaction time needed for completion in our system. Complicating catalysis or oxidative addition effects by LiI or CH$_3$Br, respectively can thus be ruled out. In addition we also prepared the oxidative addition product via the bromide-catalysed pathway and found that these crystals were the same as those reported for the structure analysis of [Ir(acac)(cod)(CH$_3$)(I)] [5].

An interesting feature of Scheme 2 is the kinetic evidence for iodomethane coordination (K_5 equilibrium) to an iridium(III) substrate. Based on the assumption that the intermediate [Ir(acac)(cod)(CH$_3$)(Br)]I$^-$ is correctly formulated, the presentation in Scheme 2 implies competition between the ligand CH$_3$I, at a much higher concentration, with the better nucleophile I$^-$ but at a much lower concentration, for coordinated bromide. The restriction for the iodomethane pathway is centered in the relative small equilibrium constant K_5 because the substitution rate of a coordinated CH$_3$I by I$^-$ compared to that for Br$^-$ is exemplified by the ratio $k_6/k_4 \sim 22$. The relatively larger k_6 value compared to k_4 is a result of the low intrinsic Lewis basicity [11] of haloalkanes. The coordination phenomenon of haloalkanes to a Lewis acid metal center, like Ir(III) in the present case, has become increasingly known through crystal structure determinations for a number of complexes since 1982 [12–15]. The detection of a CH$_3$I substitution pathway is probably in the present case ascribable to a coordinatively saturated intermediate, [Ir(acac)(cod)(CH$_3$)-(Br)]I$^-$, which results in the usual relatively slow substitution kinetics for Ir(III) and Rh(III) complexes. When a similar ionic intermediate is formed during oxidative addition from its Ir(I) square-planar precursor (i.e. in the absence of a five-coordinate Ir(I) complex), the resulting Ir(III) complex has a vacant site which substitutes at a much faster rate by I$^-$ and is thus not normally detected.

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