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Mechanism for the oxidative addition of $Hg(CN)_2$ to β-diketonato-1,5-cyclooctadieneiridium(I) complexes

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Abstract

A study has been made of the kinetics of the oxidative addition of $Hg(CN)_2$ to [Ir(β-diketone)(cod)] (cod = 1,5-cyclooctadiene) complexes in acetone. The product is [Ir(β-diketone)(cod)(CN)(HgCN)] with the CN and HgCN ligands in a *cis*-disposition. The reaction obeys a second order rate law and the electronic effects of the various β-diketone ligands were found to increase in the order acac < ba < dbm < tfa < tfba, where acac = 2,4-pentanedionato, ba = 1-phenyl-1,3-butanedionato, dbm = 1,3-diphenyl-1,3-propanedionato, tfa = 1,1,1-trifluoro-2,4-pentanedionato and tfba = 1-phenyl-4,4,4-trifluoro-1,3-butanedionato. An associative mechanism involving a cyclic three-centered addition of $Hg(CN)_2$ in the transition state is proposed.

Introduction

The oxidative addition of mercury(II) compounds to d^8 metals has been reported for a number of complexes such as, for, example, $[M(Cl)(CO)(PPh_3)_2]$ (M = Rh or Ir) [1–5]. These and other studies involving isolation of donor–acceptor complexes [6–8] between organometallic and mercury(II) compounds were not concerned with the mechanistic detail of these reactions. We recently reported [9] on the kinetics and mechanism of the oxidative addition of $Hg(CN)_2$ to [Rh(β-diketone)$(POPh_3)_2$] complexes, for which the order of rate constants was $k_{acac} > k_{tfa} \gg k_{hfa}$ (acac = 2,4-pentanedionato; tfa = 1,1,1-trifluoro-2,4-pentanedionato; hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato ligands). This is the expected result when the methyl group of acac is replaced by increasing more electronegative groups such as CF_3 in tfa or hfa, thus rendering the complex a weaker Lewis base for the attack of the $Hg(CN)_2$. NMR analyses indicated a *cis*-addition for $Hg(CN)_2$ in the oxidative addition product, which together with large negative entropy values led to a proposed cyclic three-centered transition state for this reaction. The same electronic control through varying substituents on the β-diketone ligands was applied to the present study in order to observe whether a similar mechanism and trend in reaction rates prevailed.

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Experimental

The [Ir(β-diketone)(cod)] complexes (β-diketone = 2,4-pentanedionato, acac; 1,1,1-trifluoro-2,4-pentandionato, tfa; 1-phenyl-1,3-butanedionato, ba; 1,3-diphenyl-1,3-propanedionato, dbm; 1-phenyl-4,4,4-trifluoro-1,3-butanedionato, tfba) were prepared from the dimer $[Ir(Cl)(cod)]_2$ (Strem Chemicals) by the method described previously [10], except that for the ba, dbm and tfba complexes a stoichiometric amount of the relevant ligand was allowed to react with the Ir^I dimer. ^1H NMR spectra (Bruker AM300, chemical shifts relative to TMS, $\delta = 0.0$) were recorded in C_6D_6 at 296 K. The chemical shifts for [Ir(acac)(cod)] (yellow crystals) and [Ir(tfa)(cod)] (yellow-orange crystals) have been reported before [10].

[Ir(ba)(cod)], yellow-orange crystals: δ 7.05–7.75 (m, 5H, Ph), 5.95 (s, 1H, CH), 4.38 (m, 4H, CH), 2.25 (m, 4H, CH_2), 1.77 (s, 3H, CH_3), 1.63 (m, 4H, CH_2). [Ir(dbm)(cod)], orange crystals: δ 7.08–7.81 (m, 10H, Ph), 6.74 (s, 1H, CH), 4.41 (m, 4H, CH), 2.29 (m, 4H, CH_2), 1.67 (m, 4H, CH_2). [Ir(tfba)(cod)], red crystals: δ 6.95–7.53 (m, 5H, Ph), 6.43 (s, 1H, CH), 4.30 (m, 4H, CH), 2.13 (m, 4H, CH_2), 1.50 (m, 4H, CH_2). These values agree well with those recorded in $CDCl_3$ [11].

Preparation of [Ir(acac)(cod)(HgCN)(CN)]: To a solution of [Ir(acac)(cod)] (0.2 g; 0.5 mmol) in 3 cm^3 of deoxygenated acetone was added a solution of $Hg(CN)_2$ (0.126 g; 0.5 mmol) in 1 cm^3 of acetone. The mixture was stirred under N_2 for 15 min, a fine yellow precipitate separating within ca. 2 min. The product was dried under vacuum at room temperature. A gradual darkening of the precipitate during 14 days indicated decomposition as did the elemental analysis. Found: Ir, 36.4; Hg, 21.6; C, 30.0; N, 3.78; O, 4.87; H, 3.40. $C_{15}H_{19}N_2O_2HgIr$ calc.: Ir, 29.5; Hg, 30.8; C, 27.6; N, 4.3; O, 4.90; H, 2.9%.

The IR spectra were recorded on a Hitachi model 270-50 infrared spectrophotometer with KBr optics. For the kinetic studies the reactions were monitored with a Durrum D110 stopped flow spectrophotometer at the wavelengths shown in Table 1, a thermostated (accurate to ±0.1 K) cell was used. The reactions were studied under typical pseudo-first order conditions of $1–5 \times 10^{-4}$ M [Ir(β-diketone)(cod)] with $[Hg(CN)_2]$ in 10- to 100-fold excess and acetone as solvent. (Solvent effects could not be studied owing to solubility problems.) Pseudo-first order rate constants, k_{obs}, were calculated by a linear regression program from the slopes of plots of $\ln(A_\infty - A_t)$ vs. time.

Results and discussion

Structural characterization of [Ir(acac)(cod)(HgCN)(CN)]

Chemical analysis of the oxidative addition product confirmed only the presence of mercury and nitrogen but not the stoichiometry. The IR spectra of freshly prepared samples confirmed the presence of the two expected cyanide stretching frequencies at 2135 and 2160 cm^{-1} respectively. In addition the two distinctive C⩦O and C⩦C stretching frequencies at 1538 and 1570 cm^{-1} of the β-diketonato ligand were observed. The assignment of the CN frequencies separately to the Ir–CN or Hg–CN bond is not straightforward. Since it is to be expected that the stetching frequency of a cyano group bonded directly to an iridium(III) center will vary over a wider range due to electronic control of the other ligands in the complex and that the frequency for the metal Hg–CN bond will remain more constant, we

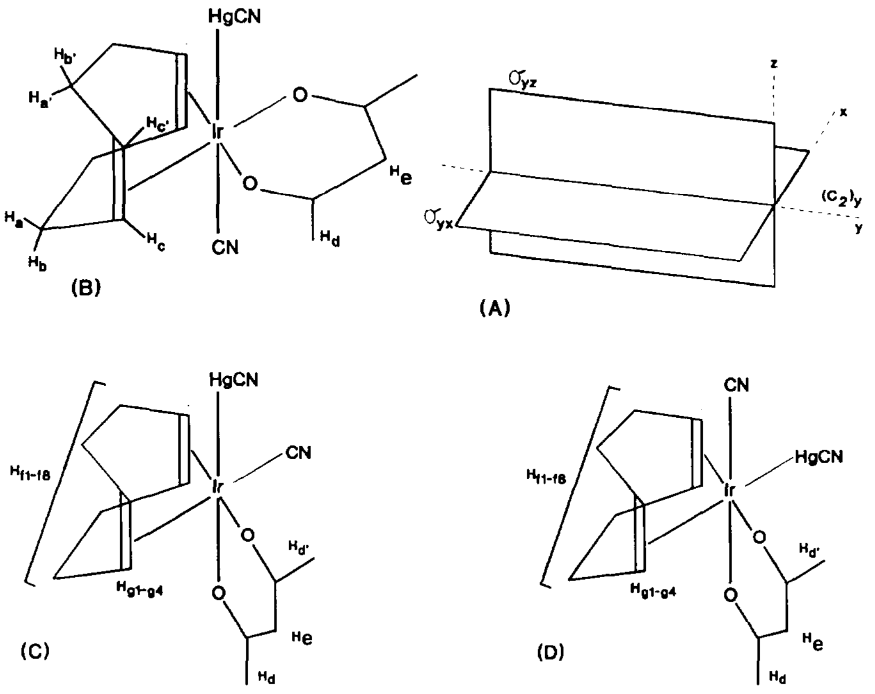


Fig. 1

compared the above frequencies with those of related complexes: [Rh(acac)$(POPh_3)_2$(HgCN)(CN)], 2136, 2164 cm^{-1} [9]; $K_3[Ir(CN)_6]$, 2185 cm^{-1} [12]; [Ir(Cl)(H)(CN)(cod)], 2190 cm^{-1} [5]; [Ir(CO)(Cl)(CN)(HgCN)(CN)$(PPh_3)_2$], 2128, 2150 cm^{-1} [2]. On the basis of these limited data we assign the bands at 2135 and 2160 to cm^{-1} ν(Hg–CN) and ν(Ir–CN), respectively. The presence of two CN stretching frequencies also confirmed that oxidative addition of $Hg(CN)_2$ had, indeed, taken place.

The question of whether the oxidative addition product contained HgCN and CN ligands in a *cis*- or *trans*-disposition was considered in the light of the ^{1}H NMR data. The [Ir(acac)(cod)] molecule should possess the symmetry elements depicted in A (Fig 1). In the case of *trans*-addition (B) the σ_{yx}-plane and C_2-axis is destroyed and its proton spectrum should give rise to eight proton signals: two methyl signals ($2 \times H_d$), one methine signal (H_e), two signals for the four vinylic cod-protons ($2 \times H_c$ and $2 \times H_c'$), and four signals for the eight methylene cod-protons ($2 \times H_a$, $2 \times H_b$ and $2 \times H_a'$, $2 \times H_b'$). The spectrum of [Ir(acac)(cod)(HgCN)(CN)] showed two non-equivalent methyl and four vinylic cod signals: δ 1.8, 2.08 (H_d, H_d'); 5.33 (H_e); 4.16, 4.52, 4.68, 5.53 (H_{g1}–H_{g4}); 3.09–2.20, 2.00–1.87 (H_{f1}–H_{f8}). This can only be reconciled with the *cis*-addition products (C or D), in which all the symmetry elements in the molecule have been lost. The NMR data do not allow a distinction between the latter two configurations.

Kinetics and mechanism

The oxidative addition of $Hg(CN)_2$ to [Ir(β-diketone)(cod)] complexes showed

Table 1

pK_a values of β-diketones, and monitoring wavelength and kinetic parameters in acetone at 25.0 °C; standard deviations in parentheses

β-Diketone	β-Diketone [a] substituents		pK_a [b]	λ (nm)	k (M^{-1} s^{-1})	$\Delta H^{\neq}$ [c] (kJ mol^{-1})	$\Delta S^{\neq}$ [c] (J mol^{-1} K^{-1})
	R_1	R_2					
acac	Me	Me	8.94	366	18.7(8)	35(1)	−100(3)
ba	Me	Ph	8.70	434	22.5(5)	33(2)	−106(5)
dbm	Ph	Ph	9.35	405	54(1)	34(2)	−95(6)
tfa	Me	CF_3	6.30	560	65(1)	30(3)	−108(9)
tfba	Ph	CF_3	6.30	405	75(5)	30(4)	−96(10)

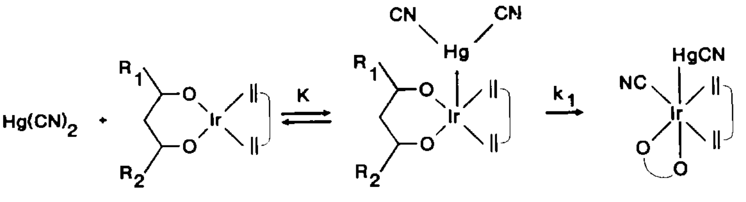
[a] Scheme 1. [b] Ref. 22. [c] From data at three temperatures.

the expected second order kinetics, i.e.:

$$\text{rate} = k\,[\text{Hg(CN)}_2]\,[\text{Ir}(\beta\text{-diketone})(\text{cod})] \qquad (1)$$

The second order rate constants and activation parameters are given in Table 1. The negative entropies of activation agree well with those for the reaction between $Hg(CN)_2$ and [Rh(β-diketone)($POPh_3$)$_2$] [9], but seem to be less negative than those for the oxidative addition of iodomethane to, for example, [Rh(cupf)(CO)(PX_3)] (cupf = anion of *N*-nitroso-*N*-phenylhydroxylamine) [13], [Rh(β-diketone)($POPh_3$)$_2$] [14] and [Ir(β-diketone)(cod)] [10] complexes. All of these reactions seem to involve a highly ordered transition state in an associative interaction of reactant molecules. The more negative $\Delta S^{\ddagger}$ values for CH_3I additions can possibly be attributed to a more polar transition state, especially in cases in which an ionic S_N2 addition mechanism was proposed. Since, as noted earlier, the addition of $Hg(CN)_2$ to [Ir(acac)(cod)] took place in *cis*-fashion, and since we did not observe any slow isomerization from a *cis*- to *trans*-configuration (such a conversion was observed for the reaction between I_2 and [Rh(β-diketone)($POPh_3$)$_2$] [15]), we favour a cyclic three-centre transition state for the k_1 step (Scheme 1).

The rate constants (Table 1) show that the presence of more electronegative substituents on the β-diketone gives rise to an increase in the reaction rate. This increase, although not significant in kinetic terms, contradicts the concept that more electronegative substituents on the β-diketone weaken the Lewis base character of the complex, which in turn should result in slower oxidative addition, observed in a number of cases [9,10,14]. However, the rate trends in Table 1 are consistent with those found for the oxidative addition of I_2 to [Rh(β-diketone)($POPh_3$)$_2$] complexes [15], where formation of a charge transfer complex in a pre-equilibrium step was



Scheme 1

followed by the oxidative addition step. Mercuric halides are known to form metal-to-mercury bonds with complexes such as (π-C_5H_5)M(CO)$_2$ (M = Co, Rh, Ir) [16,17], and the crystal structure of (π-C_5H_5)Co(CO)$_2$(HgCl$_2$) has been determined [18]. Interestingly, the Hg atom is positioned in the center of a trigonal plane made up of the Co and two Cl atoms. We suggest a similar geometry for the pentacoordinated product of the equilibrium step (Scheme 1). This would imply that oxidative addition proceeds along the k_1 step and that the path to a cyclic three-centered transition state would start from the precursor complex having the Ir–Hg–CN moiety already favourably positioned in the trigonal plane.

In accord with Scheme 1, the rate of the reaction is given by eq. 2:

$$\text{rate} = \frac{k_1 K [\text{Hg(CN)}_2][\text{Ir}(\beta\text{-diketone})(\text{cod})]}{1 + K[\text{Hg(CN)}_2]} \quad (2)$$

On the assumption that K[Hg(CN)$_2$] is $\ll 1$, this equation reduces to eq. 1 in which $k = k_1 K$. The second order rate constants (Table 1) are thus composite, and any discussion of the trends for the various β-diketones used should take account of both the complex formation constant (K) and subsequent oxidative addition rate (k_1). It is known that the tendency for a metal ion to enlarge its coordination number in a specific complex is enhanced if there is a decrease in the metal–chelate bond strength [19]. For example, the formation constants for the pentacoordinated Cu(II) complexes increase in the order [Cu(ba)$_2$ · py] < [Cu(tta)$_2$ · py] < [Cu(hfa)$_2$ · py] (tta = thenoyltrifluoroacetone) [20]. The equilibrium constant (K) in Scheme 1 should thus increase along the β-diketone series in the sequence acac < ba < dbm < tfa ≃ tfba. This is also in line with a decrease in pK_a values along the series, and it is consequently expected that tfa and tfba, with the most electronegative substituents (CF_3) should form the weakest metal–chelate bonds [21]. The expected increase in K with a decrease in the pK_a of the β-diketone in these complexes is countered by the fall in the k_1 value because of the electronic effect of the substituent (*vide supra*). The relevant magnitudes of these opposing effects will determine direction of the trend in the second order rate constants in Table 1. The increase in the observed rate constants with a decrease in the pK_a values of the β-diketones may thus be attributed to a greater increase in K relative to the expected decrease in k_1.

Acknowledgements

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