Journal of Organometallic Chemistry, 418 (1991) 241–247
Elsevier Sequoia S.A., Lausanne
JOM 22033

Kinetics of the substitution reactions of β-diketonato-1,5-cyclo-octadieneiridium(I) complexes with derivatives of 1,10-phenanthroline and 2,2′-dipyridyl

J.G. Leipoldt, S.S. Basson, G.J. van Zyl and G.J.J. Steyn
Department of Chemistry, University of the Orange Free State, Bloemfontein (South Africa)

(Received April 29th, 1991)

Abstract

The reaction between various [Ir(β-dik)(COD)] complexes and derivatives of 1,10-phenanthroline and 2,2′-dipyridyl (NN) to give the five-coordinated carbon-bonded β-diketonato complex [Ir(β-dik-C^3)(NN)(COD)] has been studied in an acetone medium. The rate constants increase from 1.36×10^1 for the acetylacetonato complex to 3.0×10^6 M^{-1} s^{-1} for the hexafluoroacetylacetonato complex. The observed rate law is $R = k[Ir(\beta\text{-dik})(COD)][NN]$. The observed linear free energy relationship (the plot of log k versus the pK_a of the β-diketone has a slope of −0.95) as well as the large negative values for the entropy of activation suggest an associative mechanism. The basicity of the incoming ligand plays only a minor role. The much higher value of k for the reaction with 2,2′-dipyridyl is attributed to the lower rigidity of 2,2′-dipyridyl. The results indicate that the rate determining step in the formation of the carbon-bonded β-diketonato complex is the associative attack of the incoming amine ligand.

Introduction

We have previously established that β-diketonatocyclo-octadiene complexes of rhodium(I), [Rh(β-dik)(COD)] are very useful in studies of the mechanism of the substitution reactions of rhodium(I) complexes for the following reasons:
(i) [Rh(β-dik)(COD)] complexes react with strong σ-donor (and weak π-bonding) ligands such as 1,10-phenanthroline by substitution of the β-diketone [1,2]:

$$[Rh(\beta\text{-dik})(COD)] + Phen \rightarrow [Rh(Phen)(COD)]^+ + \beta\text{-dik}^- \quad (1)$$

(ii) [Rh(β-dik)(COD)] reacts with π-bonding ligands such as triphenylphosphite by the substitution of the COD ligand [3]:

$$[Rh(\beta\text{-dik})(COD)] + 2P(OPh)_3 \rightarrow [Rh(\beta\text{-dik})(P(OPh)_3)_2] + COD \quad (2)$$

These two types of reactions have been successfully used to determine the effects of the substituents R_1 and R_2 of the β-diketone, $R_1COCH_2COR_2$, (and thus the bacisity of the β-diketone) on the behaviour of β-diketone as a leaving ligand [1] as well as the *trans*-effect of the β-diketone during the substitution of the COD ligand [3]. The term *trans*-effect is used although the β-diketone is a bidentate ligand since

0022-328X/91/$03.50

one of the oxygen atoms of the β-diketonato ligand must be *trans* to the rhodium–ligand bond that is broken during the first and the rate-determining step.

The reactivities of these complexes in both types of substitution reactions increase in the order acac < BA < DBM ≪ TFAA < TFBA ≪ HFAA irrespective of whether the β-diketone is the leaving or non-labile ligand, where Hacac = acetylacetone, HBA = benzoylacetone, HDBM = dibenzoylmethane, HTFAA = trifluoroacetylacetone, HTFBA = trifluorobenzoylacetone and HHFAA = hexafluoroacetylacetone. The plot of log k versus the pK_a of the β-diketone has a slope of −0.8 for the reaction of these complexes with phenanthroline [1] and −0.45 that with triphenylphosphite [3], illustrating the large influence of electronegative substituents of the β-diketone on the reactivity of these complexes.

In contrast to the reactions of the rhodium complexes, it was recently found that [Ir(acac)(COD)] reacts with 1,10-phenanthroline to give the five-coordinated carbon-bonded β-diketonato complex [Ir(acac-C^3)(COD)(Phen)] [4]. This paper deals with a kinetic study of the reaction of [Ir(β-dik)(COD)] complexes with 2,2′-dipyridyl and various derivatives of 1,10-phenanthroline [NN] with the objective of comparing the mechanism of these reactions with that for the corresponding rhodium(I) complexes. The following derivatives of 1,10-phenanthroline were used: phenanthroline (phen), 5-nitrophenanthroline (5-nitrophen), 5,6-dimethylphenanthroline (5,6-dimephen), 4,7-dimethylphenanthroline (4,7-dimephen), 3,4,7,8-tetramethylphenanthroline (3,4,7,8-tmephen). The pK_as of these ligands are listed in Table 2.

Experimental

The [Ir(β-dik)(COD)] complexes (β-dik = acac, BA, DBM, TFAA, TFBA and HFAA) were prepared from the dimer $[Ir(Cl)(COD)]_2$ as described previously [5,6].

The rate constants for all the reactions were obtained by monitoring the formation of the five coordinated complex [Ir(β-dik-C^3)(NN)(COD)] with a Durrum D110 Stopped-flow spectrophotometer at the wavelengths shown in Tables 1 and 2. All the kinetic runs were carried out in acetone medium at three temperatures. An excess of the incoming phenanthroline or dipyridyl ligand (NN) was used for all the kinetic runs in order to achieve pseudo-first-order reaction conditions, with the concentration of [Ir(β-dik)(COD)] between 2×10^{-4} and 5×10^{-4} mol dm^{-3}.

Table 1

Rate constants at 25.0 °C and activation parameters for the reaction between [Ir(β-dik)(COD)] and 1,10-phenanthroline

β-dik	λ_{exp} (nm)	pK_a [a]	k (dm^3 mol^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
acac	580	8.95	1.36×10^1	29.5	−125
BA	566	8.70	8.58×10^1	31.5	−102
DBM	580	9.35	4.13×10^2	26.3	−106
TFAA	560	6.30	1.71×10^4	24.0	−83
TFBA	550	6.30	2.51×10^4	23.1	−81
HFAA	560	4.35	3.0×10^6	–	–

[a] Reference 10.

Table 2

Rate constants at 25.0 °C and activation parameters for the reaction between [Ir(acac)(COD)] and NN

NN	pK_a	λ (nm)	k ($dm^3\ mol^{-1}\ s^{-1}$)	$\Delta H^{\ddagger}$ ($kJ\ mol^{-1}$)	$\Delta S^{\ddagger}$ ($J\ K^{-1}\ mol^{-1}$)
5-nitrophen	3.57	530	1.38	27.4	−150
phen	4.86	580	13.6	29.5	−125
5,6-dimephen	5.20	570	32.3	30.7	−113
4,7-dimetphen	5.97	620	21.9	36.5	−97
3,4,7,8-mephen	6.31	620	22.1	28.7	−122
2,2′-dipyridyl	4.30	560	116	28.2	−109

[a] Reference 20.

However, the rate constant in the case of the HFAA complex was estimated under second-order conditions (due to the very fast reaction) with [Ir(HFAA)(COD)] and [Phen] at a concentration of ca. 6×10^{-5} mol dm^{-3}.

Good linear first-order plots were obtained for at least two half-lives. The pseudo-first-order rate constants were determined for various concentrations of the incoming ligand within a ten-fold range. For all the reactions studied the plots of k_{obsd} versus [NN] (NN = various incoming amine ligands) were linear and passed through the origin. The effect of the concentration of the incoming ligand is illustrated for the reaction [Ir(TFBA)(COD)] with 1,10-phenanthroline in Fig. 1. The values of the second-order rate constants for the reaction of β-diketonato complexes with 1,10-phenanthroline and for the reaction of the acetylacetonato complex with the various incoming ligands were obtained from these plots, and are listed in Tables 1 and 2, respectively. The values of the activation parameters in Tables 1 and 2 were derived from of a non-linear least-squares the plots of rate constants against temperature by use of the Eyring–Polanyi equation.

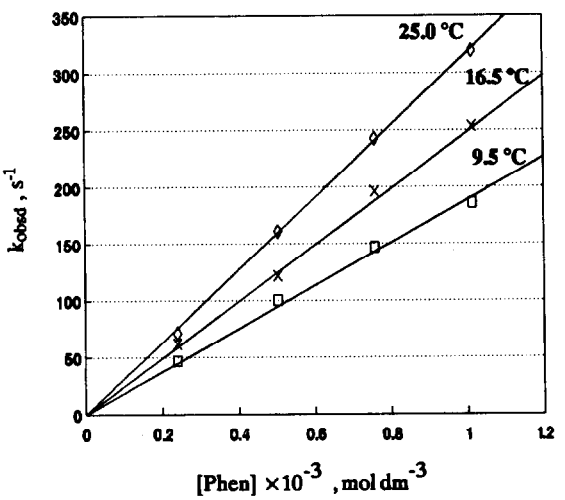

Fig. 1. Plot of k_{obsd} versus [Phen] at various temperatures for the reaction between [Ir(TFBA)(COD)] (2.5×10^{-4} mol dm^{-3}) and Phen.

Discussion

The reaction between the different [Ir(β-dik)(COD)] complexes and the various incoming ligands (NN) is represented by equation 3:

$$[\mathrm{Ir}(\beta\text{-dik})(\mathrm{COD})] + \mathrm{NN} \rightarrow [\mathrm{Ir}(\beta\text{-dik-}C^3)(\mathrm{NN})(\mathrm{COD})] \quad (3)$$

Since plots of k_{obsd} versus [NN] pass through the origin the rate law is give by equation 4:

$$\mathrm{Rate} = k[\mathrm{Ir}(\beta\text{-dik})(\mathrm{COD})][\mathrm{NN}] \quad (4)$$

The observed zero intercept (implying $k_s = 0$ in terms of the general rate law for square planar substitution reactions where rate $= (k_s + k_y\,[y])$ [substrate], [7]) is to be expected, since the displacement of any of the present bidentate ligands by a solvent molecule would be much more difficult than that of displacement of a monodentate ligand, especially in the case of a solvent with a low donocity [8].

The reactivities of the β-diketonato complexes increase in the order acac < BA < DBM ≪ TFAA < TFBA ≪ HFAA (see Table 1). The substitution of a CH_3 group of a β-diketone by the more electronegative phenyl group is accompanied by a relatively small increase in the rate constants, while the substitution of a CH_3 or a phenyl group by a more electronegative CF_3-group (the electronegativities of the substituents CH_3, phenyl and CF_3 are 2.3, 3.0 and 3.5, respectively [9]) is accompanied by a very large increase in the rate constant. The very large influence of the electronegative substituents of the β-diketone on the reaction rate is illustrated by the large slope (−0.95) of the plot of log k versus the pK_a of the β-diketone (see Fig. 2).

A possible explanation of the observed order of reactivity of these complexes is the progressive weakening of the metal–oxygen bond strength resulting from increase in the electronegativity of the substituents on the β-diketone. Such bond weakening is consistent with the observed order of the thermodynamic stability of the β-diketonato complexes of copper(II): $Cu(BA)_2 > Cu(TTA)_2 > Cu(HFAA)_2$ (HTTA = thenoyltrifluoroacetone, p$K_a = 6.3$ [10]), [11]. In keeping with this, the crystal structure determinations of [Rh(TFBA)(COD)] [12], [Rh(oxinate)(COD)] [13] and [Rh(TTA)(CO)(PPh_3)] [14] indicated that the bond between the metal and the ligand containing the most electronegative atom (or in the case of β-diketones the oxygen atom nearest to the strongest electron withdrawing substituent) is the weakest. This proposed weakening of the iridium–oxygen bond caused by electronegative substituents in the β-diketone may labilize the β-diketonato ligand. It is, however, doubtful whether this ground state effect could be responsible for the large differences in the rate constants (if $k_{HFAA}/k_{acac} = 2 \times 10^6$, see Table 1).

It is notable that the effect of the substituents of the β-diketone on the reactivity of these iridium(I) complexes towards substitution of the β-diketonato ligand and formation of the C^3-bonded β-diketonato complex is comparable to that observed for the reaction of the corresponding rhodium(I) complexes with phenanthroline (see reaction 1). The slope of log k_{obsd} versus the pK_a of the β-diketone is −0.80 for the last-mentioned reactions. This suggests that the rate determining step for the formation of the C^3-bonded β-diketonato (iridium(I) complexes) and that for the total substitution of the β-diketonato ligand (rhodium(I) complex) are probably the same. The observed linear free energy relationship, the large negative entropy values

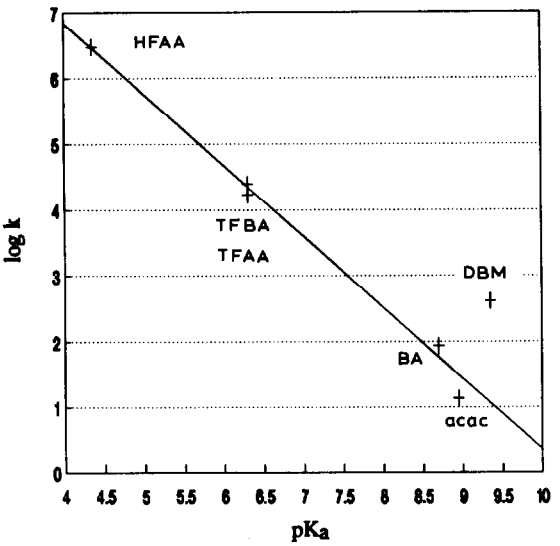

Fig. 2. Plot of log k versus the pK_a of the β-diketone, $T = 25\,^{\circ}C$.

[1] and the positive values of the volume of activation [15] all suggest an associative mechanism for the reaction of the rhodium(I) complexes. The linear free energy relationship (Fig. 2) and the large negative entropy values (Table 1 and 2) also suggest an associative mechanism for the reaction of the iridium(I) complexes.

The large influence of the substituents in the β-diketone on the reactivity of the iridium(I) complexes may thus be attributed to the ability of the electronegative groups (especially in the case of CF_3-groups) to withdraw electron density from the iridium atom and thus stabilise the five-coordinate intermediate in an associative mechanism. This stabilization of the five-coordinate intermediate is in agreement with the general experience that the ability of the central metal ion to form complexes with a higher coordination number increases with increase in the electron withdrawing ability of the chelate ring. The stability of the β-diketonato complexes of copper(II), for example, decrease in the order $Cu(BA)_2 > Cu(TTA)_2 > Cu(HFAA)_2$, showing that the increase in the acid strength of the β-diketone leads to a decrease in the thermodynamic stability of these complexes, whereas the stability of the five-coordinated adducts of these complexes with pyridine increase in the opposite sequence [11]. The effect of the electron withdrawing ability of CF_3-groups is also shown by the large decrease in the rate of the oxidative addition of CH_3I to [Ir(β-dik)(COD)] complexes from β-dik = acac to TFAA [6]. In oxidative addition reactions the metal ion act as a Lewis base; a decrease in the electron density on the metal ion caused by electron withdrawing groups would thus lead to a decrease in the reactivity of the complex in oxidative addition reactions.

For an associative mechanism one would expect that the incoming ligand would have a large influence on the reaction rate, but the basicity of the phenanthroline derivatives has a rather small effect on the rate (see Table 2). Similar results were obtained for a number of substitution reactions with an amine as entering ligand. The values of the rate constants for the reaction

$$[Pt(dipyr)Cl_2] + am \rightarrow [Pt(dipyr)(am)(Cl)]^+ + Cl^- \qquad (5)$$

increase only from 4×10^{-3} to 6.75×10^{-3} M^{-1} s^{-1} for an increase in the pK_a of the entering amine from 1.9 to 6.34, [16]. The slope of the plot of log k versus the pK_a of the amine was only 0.057. Similarly the slope of the same plot for the reaction

$$[Rh(COD)(Cl)(Pip)] + am \rightarrow [Rh(COD)(am)(Cl)] + Pip \quad (6)$$

is only 0.17, [17]. For the same phenanthroline derivatives as used in this study (see Table 2 for pK_a range), the value of the rate constants increased only from 12.4 to 29.0 M^{-1} s^{-1} for the reaction with [Rh(acac)(COD)] [2].

The relatively small effect of the basicity of the entering ligands (Table 2) does not necessarily mean that bond breaking rather than bond formation supplies the driving force for the reaction. It most probably means that the basicity of the entering ligands plays a minor role in the formation of the five-coordinated intermediate, and that the nucleophilicities of the various phenanthrolines are about the same. It should be noted that the steric effects of the different derivatives of phenanthroline should be rather similar, since we did not use an ortho-substituted phenanthroline.

The structure of the [Ir(β-dik)(COD)] complexes is such that the molecule deviates significantly from a planar geometry, the two C=C double bonds (bond length about 1.40 Å) being perpendicular to the plane of the coordination polyhedron [18]. It is thus to be expected that the reactivity of these complexes would be very sensitive to the steric effect of the entering ligand. The crystal structure of {Ir(acac)(COD)(CH_3)(I)] illustrate this steric effect of the [Ir(acac)(COD)] molecule: the H_3C–Ir–I bond angle (156.6(7)° deviates significantly from the expected 180°, with both carbon and iodine atoms displaced towards the acac ring atom plane away from the COD ligand [19]. It is notable that the reaction with 2,2′-dipyridyl (Table 2) is much faster than that with phenanthroline which has about the same pK_a. This may be attributed to the fact that although the structures of 2,2′-dipyridyl and phenanthroline suggest that they have similar steric effects, whereas 2,2′-dipyridyl is much less rigid. This rigidity of phenanthroline together with the steric hindrance caused by the COD ligand (the proposed associative activation being kept in mind) will result in a slower reaction than that of 2,2′-dipyridyl as a result of the destabilization of the five-coordinate intermediate.

Acknowledgements

The authors thank the Foundation for Research Development of South Africa and the University of the Orange Free State for financial support.

References

1 J.G. Leipoldt and E.C. Grobler, Transition Met. Chem., 11 (1986) 110.
2 J.G. Leipoldt, G.J. Lamprecht and E.C. Steynberg, J. Organomet. Chem., 402 (1991) 259.
3 J.G. Leipoldt, G.J. Lamprecht and E.C. Steynberg, J. Organomet. Chem., 397 (1990) 239.
4 L.A. Ora, D. Carmona, M.A. Esteruelas, C. Foces-Foces and F.H. Cano, J. Organomet. Chem., 258 (1983) 357.
5 G.J.J. Steyn, S.S. Basson, J.G. Leipoldt and G.J. van Zyl, J. Organomet. Chem., accepted.
6 S.S. Basson, J.G. Leipoldt, W. Purcell and J.B. Schoeman, Inorg. Chim. Acta, 173 (1990) 155.
7 F. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, 2nd ed., Wiley, New York, 1965.

8 V. Gutmann, Angew. Chem., Int. Ed. Engl., 9 (1970) 843.
9 J.E. Huheey, Inorganic Principles of Structure and reactivity, Harber and Row, New York, 1978.
10 Y. Marcus and A.S. Kertes, Ion exchange and solvent extraction of metal complexes, Wiley-Interscience, New York, 1969.
11 C.H. Ke and N.C. Li, J. Inorg. Nucl. Chem., 28 (1966) 2255.
12 J.G. Leipoldt, S.S. Basson, G.J. Lamprecht, L.D.C. Bok and J.J. Schlebusch, Inorg. Chim. Acta, 40 (1980) 43.
13 J.G. Leipoldt, E.C. Grobler, Inorg. Chim. Acta, 72 (1983) 17.
14 J.G. Leipoldt, L.D.C. Bok, J.S. van Vollenhoven and A.I. Pieterse, J. Inorg. Nucl. Chem., 40 (1978) 61.
15 J.G. Leipoldt, E.C. Steynberg and R. van Eldik, Inorg. Chem., 26 (1987) 3068.
16 L. Cattalini, A. Orio and A. Doni, Inorg. Chem., 5 (1966) 1517.
17 C.G. Nicholson and W. Robb, Inorg. Chim. Acta, 8 (1974) 41.
18 P.A. Tucker, Acta Crystallogr. Sect. B, 37 (1981) L113.
19 S.S. Basson, J.G. Leipoldt, W. Purcell and J.B. Schoeman, Acta Crystallogr., Sect. C, 45 (1989) 2000.
20 W. Robb and C.G. Nicholson, S. Afr. J. Chem., 31 (1978) 1.