Journal of Organometallic Chemistry, 397 (1990) 239–244
Elsevier Sequoia S.A., Lausanne
JOM 21086

Kinetics of the substitution of the cyclooctadiene ligand in β-diketonatocyclooctadienerhodium(I) complexes by triphenylphosphite

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(Received April 19th, 1990)

Abstract

The reaction between [Rh(β-diketonato)(COD)] complexes and triphenylphosphite was studied for various β-diketones in a dichloroethane medium. The observed rate law is $R = k[Rh(\beta\text{-diketonato})(COD)][P(OPh)_3]$. The reaction rate increases in the order acac < BA < DBM ⋘ TFAA < TFBA ⋘ HFAA (acac = acetylacetone, BA = benzoylacetone, DBM = dibenzoylacetone, TFAA = 1,1,1-trifluoro-2,4-pentanedione, TFBA = 1,1,1-trifluoro-5-phenyl-2,4-pentanedione, HFAA = 1,1,1-trifluoro-5,5,5-trifluoro-2,4-pentanedione), indicating that electronegative substituents of the β-diketone increase the reactivity of these complexes towards substitution reactions. A good linear free energy relationship was obtained. The large negative values for the entropy of activation, as well as the order of reactivity of the different β-diketone complexes, point towards an associative mechanism.

Introduction

It is well known that triphenylphosphine substitutes only one carbonyl group in complexes of the type $[Rh(LL')(CO)_2]$, where LL′ = monocharged bidentate ligands like β-diketones [1]. This phenomenon was successfully used for the determination of the relative trans-influence of the bonded atoms for a number of bidentate ligands [2–8]. Triphenylphosphite however reacts with $[Rh(\beta\text{-diketonato})(CO)_2]$ complexes with the substitution of both carbonyl groups. This characteristic may be used to synthesize complexes of the type $[Rh(\beta\text{-diketonato})(P(OPh)_3)_2]$ [9,10]. A possible explanation of this behaviour is the fact that $P(OPh)_3$ is a weaker σ-electron donor and a better π-electron acceptor than PPh_3 [11] with the result that more electron density is drawn from the rhodium(I) centre and therefore weakens the Rh–C bond in $[Rh(\beta\text{-diketonato})(CO)(P(OPh)_3)]$ relative to that in $[Rh(LL')(CO)(PPh_3)]$.

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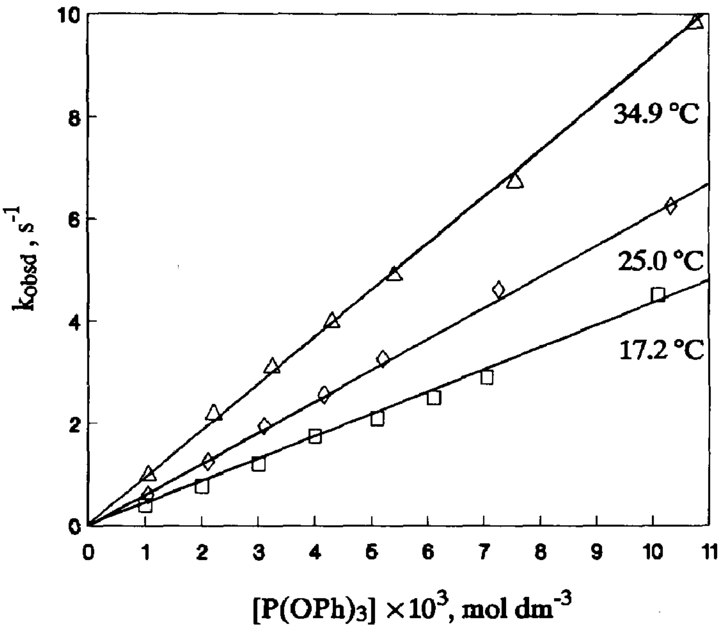

Fig. 1. Plot of k_{obsd} versus $[P(OPh)_3]$ at various temperatures for the reaction between [Rh(TFAA)(COD)] (1×10^{-4} mol dm^{-3}) and $P(OPh)_3$.

The complexes $[Rh(LL')(P(OPh)_3)_2]$ may also be synthesized by means of the reaction between [Rh(LL')(COD)] and $P(OPh)_3$ [12]:

$$[Rh(LL)(COD)] + 2P(OPh)_3 \rightleftharpoons [Rh(LL')(P(OPh)_3)_2] + COD$$

In contrast to the abovementioned reactions we observed that 1,10-phenanthroline reacts with [Rh(β-diketonato)(COD)] complexes with the substitution of the β-diketonate ion [13]. This may be explained by the fact that phenanthroline, being a weak π-acceptor, cannot substitute the COD ligand. It was thus possible to study the effect of the basicity of the β-diketone on the lability of the chelating ligand (β-diketone the leaving group) by means of a detailed kinetic study [13]. The proposed associative mechanism for this reaction was also verified by means of a high-pressure kinetic study [14].

Since $P(OPh)_3$ reacts with [Rh(β-diketonato)(COD)] complexes with the substitution of COD it is possible to study the effect of the substituents R_1 and R_2 of the β-diketone ($R_1 \cdot CO \cdot CH_2 \cdot CO \cdot R_2$) on the *trans*-effect of the β-diketone, where the latter is the non-labile ligand.

Experimental

The [Rh(β-diketonato)(COD)] complexes were synthesized as described before [13]. The product of the reaction between the [Rh(β-diketonato)(COD)] complexes and an equivalent amount of $P(OPh)_3$ in acetone was isolated by slow evaporation of the solution at room temperature. A light yellow crystalline compound was obtained in all cases. The UV-visible and infrared spectra of the products clearly indicated that these products and the products of the reaction between $[Rh(\beta\text{-diketonato})(CO)_2]$ and $P(OPh)_3$ are identical, i.e. $[Rh(\beta\text{-diketonato})(P(OPh)_3)_2]$ [9,10].

Table 1

Reaction rate constants and activation parameters for the reaction between [Rh(β-diketone)(COD)] complexes and $P(OPh)_3$

β-diketone	pKa [a]	k ($dm^3\ mol^{-1}\ s^{-1}$)	$\Delta H^{\#}$ ($kJ\ mol^{-1}$)	$\Delta S^{\#}$ ($J\ K^{-1}\ mol^{-1}$)
acac	8.95	4.84×10^1	28.4	−117
BA	8.70	5.74×10^1	30.9	−108
DBM	9.35	5.87×10^1	24.0	−130
TFAA	6.30	6.10×10^2	27.4	−99
TFBA	6.30	6.20×10^2	23.3	−113
HFAA	4.35	1.17×10^4	25.3	−82

[a] Ref. 16.

The reaction rate constants for all the reactions were obtained by following the formation of [Rh(β-diketonato)$(P(OPh)_3)_2$] at 300 nm. A Durrum stopped-flow, model D-110, spectrophotometer was used for the fast reactions and a Hitachi 150-20 spectrophotometer for the slower reactions. All the kinetic runs were performed in a 1,2-dichloroethane medium at three different temperatures (17, 25 and 35 °C). An excess of triphenylphosphite was used for all runs in order to achieve pseudo-first order reaction conditions. Freshly distilled triphenylphosphite was used.

Linear first-order plots were obtained for at least two half-lives. The pseudo-first order rate constants were determined for various triphenylphosphite concentrations (over a 10-fold range) for each β-diketone complex. The effect of the triphenylphosphite concentration on the pseudo-first order rate constant in the case of the reaction with [Rh(TFAA)(COD)] is shown in Fig. 1. The values of the second-order rate constants for the different [Rh(β-diketonato)(COD)] complexes at 25 °C together with the activation parameters are given in Table 1.

Discussion

The majority of square planar substitution reactions follow the general rate law:

$$\text{Rate} = \left(k_s + k_y[Y]\right)[\text{Complex}]$$

where k_s refers to the bimolecular attack of the solvent and k_y to the bimolecular attack of the incoming ligand, Y [15]. Plots of k_{obsd} versus $[P(OPh)_3]$ pass through the origin for all the reactions studied. The observed zero intercept ($k_s = 0$) is to be expected since the displacement of the COD ligand (which may be considered as a bidentate ligand) by a solvent (particularly a solvent with a low donosity such as 1,2-dichloroethane) would be much more difficult than the displacement of a monodentate ligand.

According to the kinetic results (see Table 1) the reactivity of the different β-diketone complexes is in the order acac < BA < DBM ≪ TFAA < TFBA ≪ HFAA (acac = acetylacetone, BA = benzoylacetone, DBM = dibenzoylacetone, TFAA = 1,1,1-trifluoro-2,4-pentanedione, TFBA = 1,1,1-trifluoro-5-phenyl-2,4-pentanedione, HFAA = 1,1,1-trifluoro-5,5,5-trifluoro-2,4-pentanedione). This order reveals the following effects of the substituents R_1 and R_2 of the β-diketone (the electronegativities of the substituents CH_3, phenyl and CF_3 are 2.3, 3.0 and 3.5 respectively [11]) on the reactivity of these complexes towards substitution reactions: (i) If a CH_3-group is substituted by a more electronegative phenyl group there is a relatively small increase in the rate constants; (ii) If a CH_3- or a phenyl group is substituted by the more electronegative CF_3-group the value of the rate constant increases significantly. The electronegative CF_3-group also has a large effect on the p*K*a-value of the β-diketone, see Table 1.

The large negative values for the entropy of activation, see Table 1, indicate that these substitution reactions proceed via an associative activation as is the case for most square-planar substitution reactions [15]. A high-pressure kinetic study also indicated that the substitution reactions of [Rh(β-diketonato)(COD)] proceed via an associative mechanism [14]. If an associative mechanism is assumed, the influence of the substituents on the reactivity of these complexes may be understood: The observed order of reactivity of the different β-diketone complexes may be explained by the general experience that a chelate ring with strong metal–ligand bonds leads to a greater thermodynamic stability while the ability of the central metal ion to form complexes with a higher coordination number increases with a decrease in the metal–chelate bond strength [16]. 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-diketones (p*K*a-value of TTA is 6.3 [17], see Table 1 for the p*K*a-values of the other β-diketones) leads to a decrease in the thermodynamic stability of these complexes. The stability of the five coordinated adducts of these complexes with pyridine however increase in the opposite sequence [18].

The increase in the acidity from acac to HFAA thus leads to the stabilization of the five coordinated rhodium(I) intermediate in an associative mechanism and consequently a higher reactivity towards substitution reactions. The large kinetic *trans*-effect caused by the electronegative CF_3-groups on the β-diketone (see Table 1 and Fig. 2) may thus be explained by the ability of this substituent to withdraw electron density from the metal ion making the complex a better electron acceptor and therefore stronger Lewis acid. The effect of the electron withdrawing ability of the CF_3-groups is also evident by the large decrease in the rate of the oxidative addition of CH_3I to $[Rh(\beta\text{-diketonato})(P(OPh)_3)_2]$ complexes from acac to HFAA [19]. In oxidative addition reactions the metal ion acts 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 reactivity towards oxidative addition reactions. The observed order of reactivity thus also points to an associative substitution mechanism. The increase in the reaction rate from the acac to the HFAA complex may also be explained by the weakening of the Rh–COD bond as a result of the electron withdrawing capability of the electronegative substituents. This ground state effect is however expected to be less important than the stabilisation of the transition state as discussed above, in determining the reactivity of the Rh-complexes.

The comparison of the kinetic results (order of reactivity of the complexes) with structural results also points to an associative mechanism: The crystal structure determination of [Rh(TFBA)(COD)] [20], [Rh(Quin)(COD)] [21], and $[Rh(Sacac)(CO)(PPh_3)]$ [8] indicate that the rhodium-ligand (ligand *trans* to the bidentate ligand) bond strength increases as a result of electronegative groups due to a decrease in the *trans*-influence of the donor atoms of the bidentate ligand. The

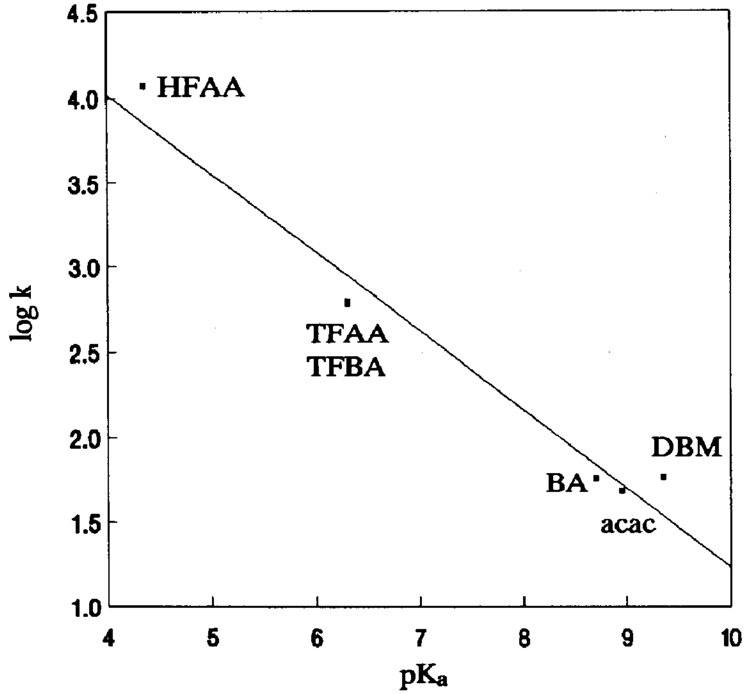

Fig. 2. Plot of log *k* versus p*K*a-values of the β-diketone, $T = 25\,°$C.

fact that the reaction rate increases with an increase in the metal–ligand bond strength thus rules out a dissociative mechanism.

The effect of the p*K*a-values of the various β-diketones is also shown in the linear free energy relationship, see Fig. 2.

The slope of the plot of log *k* versus p*K*a-value of the β-diketones is -0.45. Although this value is much less than the corresponding value for the reaction of [Rh(β-diketonato)(COD)] with 1,10-phenanthroline (-0.8) [13], it indicates that the effect of substituents of the β-diketone is approximately the same irrespective whether the β-diketone is a leaving or non-labile ligand.

Acknowledgements

We thank the FRD of the South African CSIR and the research fund of this University for financial assistance.

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