

The Oxidative Addition of Iodomethane to Acetylacetonatocarbonylphosphinerhodium(I) Complexes

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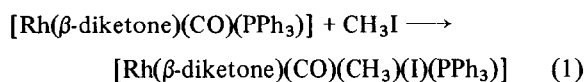
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Abstract

The kinetics and mechanism of the oxidative addition of CH_3I to $[\text{Rh}(\text{acac})(\text{CO})(\text{PX}_3)]$, where $\text{X} = p\text{-chlorophenyl}$, phenyl and $p\text{-methoxyphenyl}$, were studied with the aid of IR and visible spectrophotometry in 1,2-dichloroethane. The reaction proceeds through an initial ionic intermediate followed by two consecutive equilibrium steps, the first involving acetyl formation followed by acyl \rightarrow alkyl rearrangement to give $[\text{Rh}(\text{acac})(\text{CO})(\text{CH}_3)(\text{I})(\text{PX}_3)]$ as final product. Equilibrium and rate constants are correlated with phosphine basicity.

Introduction

We have recently reported [1] on the kinetics and mechanism of reaction (1) for β -diketones having



different electronegative substituents. These and other ligand variations usually have a marked effect on the Lewis basicity of the metal center and thus on its reactivity towards oxidative addition. We report here an extended study of this effect for $[\text{Rh}(\text{acac})(\text{CO})(\text{PX}_3)]$ complexes where $\text{X} = p\text{-chlorophenyl}$, phenyl and $p\text{-methoxyphenyl}$. These phosphines have the same Tolman [2] cone angle, but will influence the electron density on the rhodium atom differently due to the variation in electronegativity of substituents on the phenyl rings.

Experimental

The phosphines were recrystallized from EtOH before use. The starting complexes were prepared as described previously [1] except that *n*-hexane and dry diethylether were used as solvents for the tri-*p*-

chlorophenyl- and tri-*p*-methoxyphenylphosphine complexes, respectively. They were characterized by IR measurements of the $\text{Rh(I)}\text{--CO}$ wavenumbers (cm^{-1}) in 1,2-dichloroethane as solvent (KBr disk values in parentheses): *p*-PhCl 1982 (1980); Ph 1978 (1986); *p*-PhOMe 1974 (1972). The oxidative addition product $[\text{Rh}(\text{acac})(\text{CO})(\text{CH}_3)(\text{I})(\text{PPh}_3)]$ was prepared as follows. To 0.632 g $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$, partly dissolved in 25 cm^3 acetone, was added 0.5 cm^3 (five-fold excess) CH_3I . Stirring and heating ($<35^\circ\text{C}$) for 10 min gave a clear yellow solution which gradually changed to a wine-red colour. The acetone was evaporated *in vacuo* after 3 h giving a viscous red oily residue. This was dissolved in 250 cm^3 diethylether followed by evaporation up to ca. 150 cm^3 with a strong air-current. Addition of 50 cm^3 *n*-hexane gave a cloudy solution. Continued evaporation with an air-current up to ca. 150 cm^3 and storage at 0°C for 2 h gave a light brown precipitate (31% yield). *Anal.* for $\text{RhC}_{25}\text{H}_{25}\text{O}_3\text{PI}$ (calc. in parentheses): Rh, 16.30 (16.09); O, 7.40 (7.58); P, 4.78 (4.89); I, 19.7 (20.04)%.

All IR measurements were done on a Hitachi model 270-50 spectrophotometer having a wavenumber accuracy of 2 cm^{-1} in the region employed. Kinetic measurements were performed in a thermostated (0.1 K) cell with 0.5 mm path length and NaCl optics. Visible spectrophotometry was performed on a Hitachi model 150-20 spectrophotometer within the same temperature control limits. All kinetic measurements were done in 1,2-dichloroethane as solvent at 25.0°C . Typical complex concentrations were $5 \times 10^{-4}\text{ M}$ for the visible (383 nm) and 0.02 M for the IR kinetic measurements with $[\text{CH}_3\text{I}] \geq 0.1\text{ M}$. All kinetic data were fitted to the appropriate equation by using a non-linear least-squares program [3].

Results and Discussion

The general mechanistic pathway (Scheme 1) involves an initial dissociative equilibrium of the Rh(I) complex for which, in the case of $[\text{Rh}(\text{acac})\text{--}$

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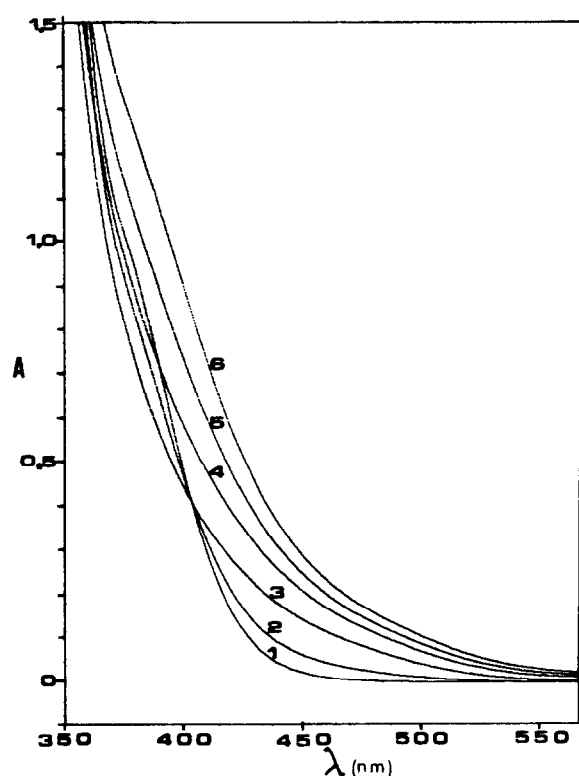
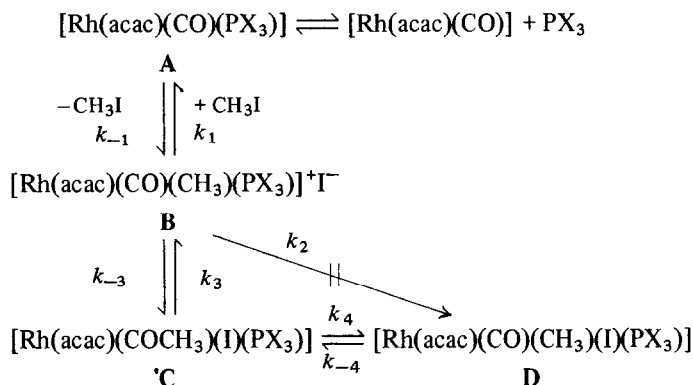


Fig. 1. Reaction progress between $[\text{Rh}(\text{acac})(\text{CO})\text{P}(p\text{-PhCl})_3]$ (6×10^{-4} M) and CH_3I (1.0 M) in 1,2-dichloroethane at 25.0°C . Curves 1 to 3 correspond to the K_1 equilibrium (Scheme 1). Time scans: (1) 0; (2) 2; (3) 10; (4) 40; (5) 75; (6) 120 min.

$(\text{CO})(\text{PPh}_3)]$, supporting evidence was obtained through rate acceleration [1] and changes in NMR spectra [4] with added free phosphine. The onset of the oxidative addition proceeds through the equilibrium step, K_1 , resulting in the postulated ionic intermediate which reacts further by different pathways to produce the final presumably trans-addition product. We previously reported values for K_1 , k_2 and k_4 in the case of $[\text{Rh}(\text{acac})(\text{CO})$ -

$(\text{PPh}_3)]$. Having used more sophisticated spectrophotometers, especially for IR measurements, we now have evidence to believe that the k_2 -path is not operative (at least for the acac complexes) and that the previously determined k_2 value should be considered as a k_3 constant; i.e., the formation of the final oxad product proceeds solely through the intermediate acyl complex C (Scheme 1).

Typical absorbance-time traces at 382 nm for the reaction progress of these acac complexes showed three distinctive phases: a short induction period (ca. 1–10 min), a slow increase in absorbance (up to ca. 30 min) and a still slower increase for the last phase. Since the induction period was less than ca. 3 min for $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$, we previously reported only a biphasic absorbance-time plot at 450 nm for this compound's reaction progress. However, having used $\text{P}(p\text{-PhCl})_3$ instead of PPh_3 , we now could retard the induction period to the extent shown in Fig. 1. All three acac complexes have an isosbestic point at 400 nm for this induction period. With an initial decrease in absorbance at 382 nm we found that the observed pseudo-first-order rate constants (for $[\text{CH}_3\text{I}] = 0.1\text{--}0.5$ M) fitted eqn. (2),

$$k_{\text{obs}} = k_1[\text{CH}_3\text{I}] + k_{-1} \quad (2)$$

from which values for k_1 , k_{-1} and K_1 were obtained (Table I).

Repeated IR time scans showed that for the duration of the induction period this equilibrium involved a near complete disappearance of the $\text{Rh}(\text{I})\text{--CO}$ peak and the simultaneous appearance of a $\text{Rh}(\text{III})\text{--CO}$ peak ascribable to that of the ionic intermediate, B (Scheme 1). Observed rate constants obtained from the disappearance of the $\text{Rh}(\text{I})\text{--CO}$ peaks (Table II) correspond well with k_{obs} values calculated (by means of eqn. (2)) from the data in Table I. The acyl peaks, observed at 1724 cm^{-1} in all cases, formed at nearly the same (for $\text{X} = p\text{-PhCl}$) or at progressively slower rates (for the more basic phosphines) compared to that of the corresponding $\text{Rh}(\text{III})\text{--CO}$ peaks of B. When the latter started to

TABLE I. Rates and Equilibrium Constants for the Oxidative Addition of CH₃I to [Rh(acac)(CO)(PX₃)] Complexes (Standard Deviations in Parentheses)

X	$k_1 \times 10^3$ (M ⁻¹ s ⁻¹)	$k_{-1} \times 10^4$ (s ⁻¹)	K_1 (M ⁻¹)	$k_3 \times 10^3$ (s ⁻¹)	$k_4 \times 10^4$ (s ⁻¹)
<i>p</i> -chlorophenyl	3.46(0.09)	8.6(1.2)	4.0(0.2)		0.98(0.03)
phenyl	23.5(2.8)	25(2)	9.4(1.3)	6.5(0.4) ^a	2.1(0.2)
<i>p</i> -methoxyphenyl	138(3)	88(12)	16(2)	9(3)	

^aRef. 1.TABLE II. Infrared Carbonyl Wavenumbers and Rate Constants for Oxidative Addition of 0.5 M CH₃I to [Rh(acac)CO)(PX₃)] Complexes (Standard Deviations in Parentheses)

X	CO Wavenumbers		$k_{\text{obs}} \times 10^3$ (s ⁻¹)	$k_3 \times 10^3$ (s ⁻¹)	$k_4 \times 10^4$ (s ⁻¹)
	Complex B ^a	Complex D ^a	(disappearance of A) ^a	(formation of C) ^a	(disappearance of C) ^a
<i>p</i> -chlorophenyl	2076	2064	2.41(0.06)	2.4(0.2)	1.41(0.04)
phenyl	2072	2060	12(1)	6.3(0.5)	4.3(0.1)
<i>p</i> -methoxyphenyl	2068	2056	36(2)	9.2(1.7)	4.0(0.2)

^aRefer to complexes in Scheme 1.

disappear the acyl peak was still increasing to a near maximum absorbance value. The time required for the latter process coincided with the absorbance increase immediately following the induction period of the visible spectra. The k_3 values were determined from the earliest possible acyl peak formations in the IR, as well as from the linear reciprocal plots of eqn. (3) for the data obtained in the visible region.

$$k_{\text{obs}} = \frac{k_3 K_1 [\text{CH}_3\text{I}]}{1 + K_1 [\text{CH}_3\text{I}]} \quad (3)$$

Equation (3) could not be applied for X = *p*-PhCl due to roughly equal k_{obs} values in the A → B and B → C conversions (Table II). The k_{obs} values obtained from the visible spectra for the remaining complexes were found the most reliable at conversions of ca. 50% and more along the k_3 path. Absorbance–time data, collected at the isosbestic points (400 nm), also confirmed the latter as the most appropriate procedure.

The final and much slower disappearance of the acyl peak led to the formation of a second Rh(III)–CO peak to the order of 12 cm⁻¹ lower than the previous one (complex B) for each of the complexes (Table II). This peak formation corresponds to the final oxidative addition product, D. The k_4 constants, determined from the acyl peak disappearance (Table II), are in fair agreement with those in Table I.

The equilibrium data in Table I show a forty-fold increase in k_1 values and a four-fold increase in the equilibrium constants, which is indirectly related to the σ-donor ordering of P(*p*-PhOMe)₃ > PPh₃ > P(*p*-PhCl)₃ and thus also to the relative basicity of the

respective rhodium complexes toward oxidative addition. The carbonyl wavenumbers (Table II), being also a function of the electron density on rhodium, display the same metal basicity trend. The constant lowering of 12 cm⁻¹ from the ionic intermediate to the final oxad product in each case must be ascribed to a constant addition of electron density to the rhodium atom through coordination of the I⁻ ligand. This effect is reconcilable with a lower coordination number five for the ionic intermediate B.

Both the k_3 and k_4 values show a very moderate increase with increasing Lewis basicity of the PX₃ ligand. The k_3 path, as mentioned before [1], is assumed to comprise a rate-determining methyl group migration to CO followed by a fast nucleophilic attack by I⁻ on the resulting acetyl cation, since free added *N*-methylpyridinium iodide had no catalyzing effect on the observed reaction rate. It is also known that added nucleophiles, like phosphines, enhance CO insertion rates [5]. Having a constant incoming nucleophile in the form of I⁻ in the present case, it is only the different σ-donating properties of the coordinated phosphines which will fulfill the role of nucleophilic enhancement of CH₃ migration. The fact that the k_3 route is preferred over the more direct k_2 path can be attributed to the well-known strong *trans* labilizing effect of the CH₃ group. Bond formation of I⁻ *trans* to the CH₃ group (implying the k_2 path) especially in a square pyramidal array of the ionic intermediate, B, should be more difficult in comparison with a solvated transient acetyl cation [Rh(acac)(COCH₃)(PX₃)(solv)_x]⁺

for the k_3 path. Dielectric constant related solvent effects observed previously [1] emphasized the importance of stabilization of these ionic species. The five-coordinate $[\text{Rh}(\text{acac})(\text{COCH}_3)(\text{PX}_3)(\text{I})]$ is similarly believed to contain a weakly coordinated solvent molecule since a nucleophilic substitution study [6] of the PPh_3 derivative gave mechanistic evidence of a solvent-assisted equilibrium. The k_4 values listed should thus be strictly considered as k_{obs} values in the process of attaining equilibrium proceeding from the acetyl to σ -methyl derivative. In this context care was taken to obtain rate constants at the earliest possible stages of acyl \rightarrow alkyl conversions. It was also noted previously [1] that both complexes exist in IR detectable quantities at infinite reaction times in neat CH_3I as solvent, stressing the existence of the K_4 equilibrium. This equilibrium was probed further by IR monitoring of a 1,2-dichloroethane solution of $[\text{Rh}(\text{acac})(\text{CO})(\text{CH}_3)(\text{I})(\text{PPh}_3)]$. It showed a gradual decrease of the Rh(III)-CO peak and a simultaneous growth in the acyl peak with time. When the latter tended to equilibrate, the Rh(I)-CO peak started to appear at the appropriate wavenumber. At longer reaction times (ca. 60 h) the solution spectrum showed an equilibrium mixture of complexes **A**, **C** and **D**. This as well as the noticeable upward shift of the Rh(III)-CO wavenumber, intermediate to those of **B** and **D**, confirmed the complete solvent-assisted reversibility of the system. A reaction run in 0.5 M CH_3I retarded the formation of **A**, as was expected, and also yielded $k_{-4} = 2.7(1) \times 10^{-5} \text{ s}^{-1}$ based on the first ca. 10% conversion of the Rh(III)-CO peak. Thus $K_4 = 7.8(8)$ using the k_4 value in Table I. This k_4 value (Table I) is the average of twelve separate runs and is believed to be more reliable than the single estimate of Table II. The

k_4 constants increase roughly four-fold from the *p*-chlorophenyl to *p*-anisyl complexes whilst the reverse trend, based on the phosphine basicities [7] and as observed to a small extent in the decarbonylation of *trans*- $[(\text{h}^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{L})(\text{COCH}_3)]$ (L = a tertiary phosphine) [8], was expected.

Both the k_3 and k_4 pathways are retarded by making the 16 electron ionic intermediate (**B**) or acetyl complexes (**C**) more electron deficient by using weaker σ -donating phosphines. It would be interesting to observe this effect in more detail for the hexafluoroacetylacetonato complexes, since previous work has shown the absence of acetyl formation during reaction progress. It may be that a much slower k_2 route would operate under such circumstances.

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