Determination of the free activation energy for the breaking of the ^{31}P–$^{107(109)}Ag$ bond in $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-pz})_3Ag(PPh_3)]$

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(Received July 9, 1993)

Abstract

The Arrhenius equation corresponding to the process P–Ag + P*–Ag* → P–Ag* + P*–Ag has been determined for $[(\eta^6\text{-}p\text{-cymene})Ru(\mu\text{-pz})_3Ag(PPh_3)]$ (1) by complete line-shape analysis of the ^{31}P NMR spectra between −40°C and +30°C. It has the form $k = 10^{11.8 \pm 1}\, e^{(-46 \pm 5\ \mathrm{kJ\ mol^{-1}}/RT)}$. The preexponential term, log A = 11.8 corresponds to a small activation entropy, whereas the activation energy, 46 kJ mol^{-1}, is comparable to those determined for other phosphorus–metal compounds.

Key words: Silver; Ruthenium; Phosphorus; Nuclear magnetic resonance

1. Introduction

The bond between phosphorus and silver can break with a low activation energy which corresponds to the range of energy barriers that can be determined by NMR spectroscopy. Information about this barrier comes from classical kinetics experiments on the following reaction [1].

$$[Ag(hfacac)PPh_3(soln)] + PPh_3(soln) \longrightarrow [Ag(hfacac)(PPh_3)_2](soln) \quad (1)$$

In this reaction the activation energy −49.0 kJ mol^{-1} (solvent, dichloromethane) can be taken as the negative value of the Ag–PPh_3 bond-dissociation energy in solution. Muetterties and Alegranti [2] have determined the E_a for Ag–P bond rupture in silver(I) complexes using coalescence temperature and line-shape analysis for ^{31}P NMR spectra recorded at 40.5 MHz. For $[L_4AgNO_3]$, with $L = (C_6H_5CH_2)_3P$, $E_a = 38 \pm 4$ kJ mol^{-1}, and for $[L'_4AgClO_4]$, with $L' = (C_2H_5O)_3P$, $E_a = 46 \pm 4$ kJ mol^{-1}. These values are approximate because the temperatures were determined only to ±6°C. Moreover, the presence of two different silver isotopes, ^{107}Ag and ^{109}Ag, was apparently not taken into account in the lineshape analyses. Because added phosphorus compound did not alter detectably the ligand exchange rate and because of the absence of any marked anion effect (Cl^-, NO_3^-, PF_6^-, or ClO_4^-), Muetterties and Alegranti concluded that the mecha-

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0022-328X/94/$7.00
SSDI 0022-328X(93)24178-8

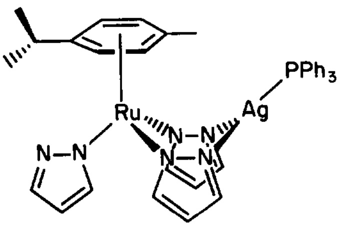
nism is S_N1-like and that the rate-determining step is ligand dissociation, where $k_1 \ll k_2$.

$$[L_4Ag]^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [L_3Ag]^+ + L^- \qquad (2)$$

We have found [3] that [(η^6-*p*-cymene)Ru(μ-pz)$_3$Ag(PPh$_3$)] (**1**) shows dynamic behaviour in ^{31}P NMR spectroscopy. Therefore, we decided to determine the P–Ag bond-rupture activation energy using improved NMR-line-shape theory.

2. Results and discussion

Complex **1** has been prepared by reaction of [{AgCl(PPh$_3$)}$_4$] [4] with [(η^6-*p*-cymene)Ru(pz)$_2$(Hpz)] [5] in the presence of KOH. Its structure has not been determined, but by analogy with the complex [(η^5-C$_5$Me$_5$)Ir(μ-pz)$_3$Ag(PPh$_3$)] [6] we propose that the compound has a ground state such as **1**.



(**1**)

A series of ^{31}P (proton decoupled) NMR spectra of compound **1** dissolved in CDCl$_3$ at a concentration of *ca.* 0.015 mol l^{-1} was recorded at 121.4 MHz as a function of temperature. A typical selection of superposed experimental and calculated spectra are shown in Fig. 1. At −50°C two doublets centred at 15.8 ppm with $^1J(^{31}P-^{107}Ag) = 565.2$ Hz and $^1J(^{31}P-^{109}Ag) = 652.8$ Hz (ratio 1.155) are observed. As the temperature increases, the lines broaden and coalesce into a single line at 15 ppm. A series of spectra was recorded at −50°C, −40°C, −30°C, −20°C, −10°C, −5°C, 0°C, 5°C, 30°C, and 55°C.

The observed lineshape changes indicate the overall degenerate exchange process (eqn. (3)) characterized by the rate constant, *k*.

$$P{-}Ag + P^*{-}Ag^* \overset{k}{\rightleftharpoons} P{-}Ag^* + P^*{-}Ag \qquad (3)$$

Equation (3) represents the following isotopic reactions.

$$P{-}^{107}Ag + P^*{-}^{107}Ag^* \overset{k_{aa}}{\rightleftharpoons} P{-}^{107}Ag^* + P^*{-}^{107}Ag \qquad (4)$$

$$P{-}^{109}Ag + P^*{-}^{109}Ag^* \overset{k_{bb}}{\rightleftharpoons} P{-}^{109}Ag^* + P^*{-}^{109}Ag \qquad (5)$$

$$P{-}^{107}Ag + P^*{-}^{109}Ag^* \overset{k_{ab}}{\rightleftharpoons} P{-}^{109}Ag^* + P^*{-}^{107}Ag \qquad (6)$$

Here a refers to $^{31}P-^{107}Ag$, b to $^{31}P-^{109}Ag$, J_a and J_b are the coupling constants and x_a and x_b, the respective mole fractions ($x_a + x_b = 1$). These reactions are characterized by the group-exchange rate constants $k_{aa} = k.x_a$, $k_{ab} = k.x_b$, $k_{ba} = k.x_a$ and $k_{bb} = k.x_b$.

In order to calculate the NMR lineshapes of ^{31}P nuclei bound to silver when the reactions listed in eqns. (3) to (6) occur, the quantum mechanical density matrix formalism adapted for a network of superposed intermolecular exchange reactions [7] had to be employed. Taking into account the rules described in ref. 7, the Liouville matrix $\mathscr{L}$ (ν_P being the chemical shift of ^{31}P) and the exchange matrix $\mathscr{K}$ ($\mathscr{K}$ is visualized in Scheme 1) for the system studied were found to be given by the equations (7) and (8).

$$\mathscr{L} = \begin{vmatrix} \nu_P + (J_a/2) & & & \\ & \nu_P - (J_a/2) & & \\ & & \nu_P + (J_b/2) & \\ & & & \nu_P - (J_b/2) \end{vmatrix} \qquad (7)$$

$$\mathscr{K} = \begin{vmatrix} -(k_{aa}/2) - k_{ab} & k_{aa}/2 & k_{ba}/2 & k_{ba}/2 \\ k_{aa}/2 & -(k_{aa}/2) - k_{ab} & k_{ba}/2 & k_{ba}/2 \\ k_{ab}/2 & k_{ab}/2 & -(k_{bb}/2) - k_{ba} & k_{bb}/2 \\ k_{ab}/2 & k_{ab}/2 & k_{bb}/2 & -(k_{bb}/2) - k_{ba} \end{vmatrix} \qquad (8)$$

The population vector is then as shown in (9).

$$x = \begin{pmatrix} x_a/2 \\ x_a/2 \\ x_b/2 \\ x_b/2 \end{pmatrix} \qquad (9)$$

As usual, the relaxation matrix $\mathscr{R}$ was taken as diagonal, with the elements given by $-1/T_2 = \pi\, W_0$, W_0/Hz being the line width in the absence of exchange.

A PC-based computer program was written for this particular problem. The isotopic mole fractions x_a and x_b of ^{107}Ag and ^{109}Ag were taken as 0.5182 and 0.4818 [8]. Only the coupling constant $J_a = J(^{31}P-^{107}Ag)$ needed to be adapted since $J_b = J(^{31}P-^{109}Ag) = J_a\gamma\, ^{109}Ag/\gamma\, ^{107}Ag$, where the gyromagnetic ratio is given by $\gamma\, ^{109}Ag/\gamma\, ^{107}Ag = 1.1496$ [8]. W_0 was taken from the spectra at −50°C and kept constant at 5.80 Hz during the simulations of the spectra recorded at higher temperatures.

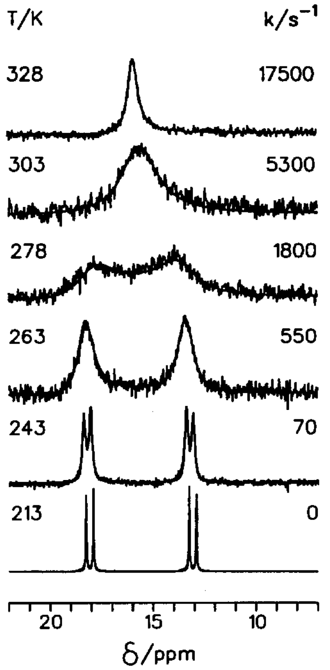


Fig. 1. Superimposed experimental and calculated ^{31}P NMR spectra of 1 at 80.9 MHz as a function of temperature.

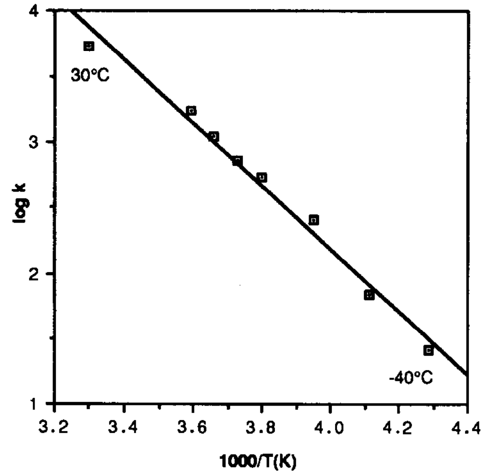
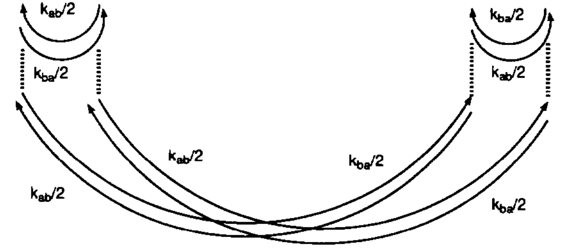


Fig. 2. Arrhenius plot for compound 1 (temperatures used: −40°C to +30°C).

Figure 1 shows the good fit of the experimental and the calculated spectra. In order to improve the fit, the phase of the calculated spectra was adapted to the experimental signal phase. The Arrhenius diagram obtained is shown in Fig. 2. The temperature-dependence of the rate constants can be expressed by $k = 10^{11.8 \pm 1} e^{(-46 \pm 5 \text{ kJ mol}^{-1}/RT)}$. The margins of error are of purely statistical origin and do not include possible systematic errors. The Eyring treatment using all values between −40°C and +30°C (8 points) yields $\Delta H^{\ddagger} = 44$ kJ mol^{-1} and $\Delta S^{\ddagger} = -26$ J K^{-1} mol^{-1}.



Scheme 1.

3. Conclusions

The activation energy, 46 ± 5 kJ mol^{-1} for the P–Ag rupture process of compound 1 in $CDCl_3$ compares well with the values of 49, 38 and 46 kJ mol^{-1} reported [1,2]. However, the last values are only approximate because of problems with temperature measurement and lineshape analysis, as discussed above. Therefore, no reliable activation entropies have been obtained until now [1,2]. Nevertheless, the related rupture of the P–Ru bond has been followed by classical kinetics using time-dependent ^{31}P NMR spectroscopy [9] and activation parameters were reported for compounds of the type $[(\eta^5\text{-}C_5Me_5)RuX(PMe_3)_2]$. Depending on the nature of X, values of $\Delta H^{\ddagger}$ between 100 and 200 kJ mol^{-1} and of $\Delta S^{\ddagger}$ between 38 and 120 J K^{-1} mol^{-1} were obtained [9]. As expected for a process which can be studied by classical kinetics, these activation enthalpies are much larger than those obtained here by lineshape analysis. More surprising is that the $\Delta S^{\ddagger}$ values of the P–Ru dissociation are positive whereas the value found here for the P–Ag dissociation is slightly negative. In order to confirm and interpret this, further experiments will be necessary, in which the solvent and the substrate concentrations are varied systematically and where rate constants are obtained using magnetization transfer experiments over a larger temperature range. At present, one can only speculate and discuss this result in terms of either an S_N2 process, an "early" transition state of the Ag–P bond breaking process, or a complicated molecular-structural change associated with the dissociation.

Since the negative $\Delta S^\ddagger$ value may indicate an associative process, the spectra were recorded with added PPh_3 present. Under these conditions only one ^{31}P NMR signal was observed, its chemical shift being the average weighted value between that of **1** and that of free PPh_3, and an acceleration of the dynamic process was observed. Thus, for a 1:1 mixture of **1** and PPh_3, at 121.4 MHz, a slightly broadened singlet ($\delta = 4.04$ ppm) was found at 243 K (compare with Fig. 1). These experiments strongly support a PPh_3-catalyzed process catalyzed by "adventitious" PPh_3.

4. Experimental details

The ^{31}P NMR spectra were recorded in $CDCl_3$ at 121.4 MHz (7.05 Tesla) with a Varian Unity 300 spectrometer. Temperature readings were accurate to ±0.5°C (the thermometer was calibrated against the ^{1}H NMR spectra of methanol). The FID was transformed to ASCII code in order to be analyzed and simulated on a PC. The reference was 85% H_3PO_4 in D_2O. The C, H and N analyses were carried out with a Perkin-Elmer 240-C microanalyzer. Solvents used for the preparation of **1** were dried and distilled before use.

4.1. Preparation of [η^6-p-cymene)Ru(μ-pz)$_3$Ag(PPh$_3$)] (1)

Under dinitrogen, [{AgCl-(PPh_3)}$_4$] (120.5 mg, 0.30 mmol) and KOH (1.90 cm^3, 0.16 mol dm^{-3}, 0.30 mmol) in MeOH were added to a solution of [η^6-*p*-cymene)Ru(pz)$_2$(Hpz)] (130.0 mg, 0.30 mmol) in the same solvent. After stirring for 45 min the resulting yellow solution was evaporated to dryness *in vacuo*. The residue was extracted with dichloromethane (20 cm^3) and the solution concentrated under reduced pressure. The addition of hexane gave a yellow solid which was filtered off, washed with hexane and air-dried. Yield: 75%. Anal. Calcd. for $C_{37}H_{38}AgN_6Ru$: C, 55.09; H, 4.75; N, 10.42. Found: C, 55.32; H, 5.08; N, 10.09%. ^{1}H NMR ($CDCl_3$, 300 MHz, r.t., δ): 0.97 (d, 6H, $^3J_{HH} = 6.9$ Hz), 1.46 (s, 3H), 2.17 (s, 1H), 5.26, 5.59 (AB system, 4H, $J_{AB} = 6.0$ Hz), 6.08 (broad, 3H), 6.61 (broad, 3H), 7.2–7.8 (m, 18H).

Acknowledgment

We are indebted to Professor J.A. Martinho Simoes (Inst. Sup. Técnico, Dep. Engenharia, Lisbon, Portugal) for calling our attention to ref. 1.

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