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Phosphine exchange at *trans*-$Pt(SnPh_3)_2(PMe_2Ph)_2$

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Phosphine exchange at square-planar *trans*-$Pt(SnPh_3)_2(PMe_2Ph)_2$ has been studied by ^{31}P NMR spectroscopy as a function of ligand concentration and temperature in C_6D_6 using magnetisation transfer techniques. Exchange of a specific phosphine takes place according to a second order rate law with $k_{ex}^{298} = 33.1 \pm 3$ dm^3 mol^{-1} s^{-1}, $\Delta H^‡ = 24.4 \pm 7$ kJ mol^{-1} and $\Delta S^‡ = -131 \pm 23$ J K^{-1} mol^{-1}. The highly negative activation entropy and the rate law indicate an associative mode of activation. In spite of the overall large steric requirements of the four tertiary ligands the activation parameters indicate a fairly closed transition state, possibly due to an electronic stabilisation of the transition state by the π-acidic stannyl ligands.

Introduction

Substitution in square-planar complexes has been studied thoroughly and normally follows the well known associative pattern with a two-term rate law.[1] However, in recent years it has become clear that dissociative substitution is a viable alternative in complexes with strongly σ-donating Group 14 hydrocarbyl or silyl ligands.[2,3] In Group 14 and 15 the ground state *trans* influence is the highest for P- and Si-donors and it decreases on going down the groups. At the same time, the π acidity of the ligands presumably increases, increasing the stability of the associative transition states.[4] This manifests itself in the high *trans* effect of triphenylstibine and trichlorostannyl ligands.[5,6] To our knowledge, there are no quantitative studies of substitution reactions in stannylplatinum complexes and we therefore thought it of interest to investigate such a process.

Kinetic studies on exchange reactions in square-planar platinum(II) complexes have mostly been performed for PtS_4^{2+} species,[7] but there are a few examples of studies of *cis*- and *trans*-PtX_2L_2 complexes including associative and dissociative pathways.[1c,3,8] Generally, studies of associative phosphine exchange are scarce and have mostly been done in the context of geometrical isomerisation. The data that exist point towards *cis* complexes reacting much faster than *trans* complexes.[8]

In the present work we have studied phosphine exchange at *trans*-$Pt(SnPh_3)_2(PMe_2Ph)_2$ as a function of ligand concentration and temperature.

Experimental

General considerations

Solvents were dried with and stored over molecular sieves. *trans*-$Pt(SnPh_3)_2(PMe_2Ph)_2$ **1** was prepared from the carbonatobis(phosphine) complex of Pt^{II} and triphenyltin hydride according to Eaborn *et al.* and its spectral features were in agreement with the literature.[9] All other chemicals and reagents were purchased and used as received.

NMR measurements

NMR spectra were recorded on a Varian UNITY 300 spectrometer working at 299.78 (^1H) or 121.35 (^{31}P) MHz. Chemical shifts are given in ppm downfield from TMS (^1H δ 0) or H_3PO_4 (^{31}P δ 0) using an external reference. The samples were (3–6) × 10^{-3} mol dm^{-3} solutions of **1** in C_6D_6 containing (3–208) × 10^{-3} mol dm^{-3} of the ligands. The kinetics of phosphine ligand exchange was measured using magnetisation transfer (MT) ^{31}P NMR spectroscopy. In an experiment the peak from the free phosphine was selectively inverted using the DANTE pulse sequence[10] and after a pulse-mixing time varying between 10 μs and 40 s a FID (free induction decay) was recorded with a non-selective π/2 pulse. During the FID ^1H decoupling was applied. Typically, 16 spectra with different pulse mixing times varying between 10 μs and 40 s were recorded. Each spectrum was collected as 500–800 repetitions with a relaxation delay.

Above room temperature a slow decomposition of complex **1** could be observed. This decay amounts to 10–30% of the initial concentration after *ca.* 30–40 h and in the kinetics at 308 and 318 K it was corrected for by applying a linear correction function.

Results and discussion

Exchange kinetics

Exchange of PMe_2Ph at *trans*-$Pt(SnPh_3)_2(PMe_2Ph)_2$, reaction (1), was studied by means of ^{31}P magnetisation transfer NMR

$$\begin{aligned}&trans\text{-}Pt(SnPh_3)_2(PMe_2Ph)_2 + n{*}PMe_2Ph \rightleftharpoons \\ &trans\text{-}Pt(SnPh_3)_2(PMe_2Ph)_{2-n}({*}PMe_2Ph)_n + nPMe_2Ph \qquad (1)\end{aligned}$$

spectroscopy as a function of free phosphine concentration and temperature in benzene-d_6 solvent. A ^1H decoupled ^{31}P spectrum of **1** and PMe_2Ph consists of one singlet from the free phosphine at δ −43 and one from **1** at δ −15.4 with platinum and tin satellites ($^1J_{Pt\text{-}P} = 2445$, $^2J_{Sn\text{-}P} = 174$ Hz). In an experiment the peak of the free phosphine was selectively inverted and the integrals of both the coordinated and the free phosphine were recorded as a function of pulse mixing time; the time-dependent integrals were then recalculated to deviations from equilibrium. The reaction was treated as a two-site exchange according to eqn. (2). The return of magnetisation to equilibrium is governed by the exchange rate constants, k_F and k_C, and the relaxation rate constants $1/T_{1F}$ and $1/T_{1C}$.[11] Taking

$$P_{free} \underset{k_C}{\overset{k_F}{\rightleftharpoons}} P_{coord} \qquad (2)$$

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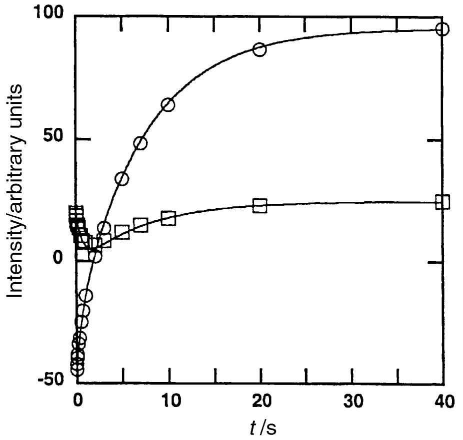

Fig. 1 Magnetisation of free (○) and coordinated (□) phosphine in reaction (2) as a function of pulse mixing time. The solid lines were calculated using the parameters from the best fit and the computer program CIFIT.[17] [Pt] = 6.3 × 10^{-3} mol dm^{-3}, [Me_2PhP] = 23.5 × 10^{-3} mol dm^{-3}, T = 298.0 K, k_C = 0.935 s^{-1}, T_{1F} = 9.8 s, T_{1C} = 3.5 s.

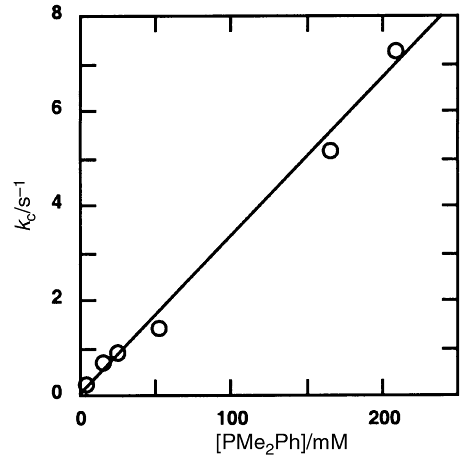

Fig. 2 Pseudo first-order exchange rate constants of reaction (1) as a function of dimethylphenylphosphine concentration. The solid line denotes the best linear least-squares fit giving a second order rate constant of 33.1 dm^3 mol^{-1} s^{-1} at T = 298.0 K.

into account the fact that $k_F = k_C[P_{coord}]/[P_{free}]$, this model was fitted iteratively to the time dependent magnetisation deviation data using the computer program FACSIMILE.[12] A typical plot is given in Fig. 1. After correction for decomposition at the two higher temperatures (see above) all data were fitted well by this model.

The value of k_C thus obtained corresponds to an observed pseudo first-order rate constant for the exchange of a specific phosphine, giving the rate equation (3), where R_{ex} is the total

$$R_{ex} = 2\,k_C[\mathrm{Pt}] = k_C[\mathrm{P_{coord}}] \qquad (3)$$

rate of exchange. A plot of k_C *vs.* free phosphine concentration is linear with zero intercept as shown in Fig. 2. The overall rate law is thus (4) where k_{ex} is the second-order rate constant for

$$R_{ex} = 2\,k_{ex}[\mathrm{PMe_2Ph}][\mathrm{Pt}] \qquad (4)$$

exchange of a specific phosphine. The temperature dependence of k_{ex} was determined giving the Eyring plot in Fig. 3. Owing to experimental limitations (decomposition and the dynamic range of MT experiments) the accessible temperature interval was only 20 degrees. To ensure a reasonable accuracy of the second order rate constants they were computed using at least two different concentrations. Activation parameters are $\Delta H^‡$ = 24. ± 7 kJ mol^{-1} and $\Delta S^‡ = -131 \pm 23$ J K^{-1} mol^{-1}. The errors quoted are based on the scattering of all 11 individual data points. Values of k_C as a function of temperature and concentration are given in Table 1.

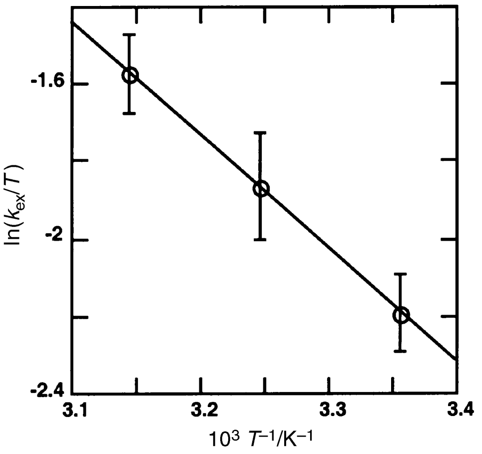

Fig. 3 Eyring plot for exchange of a specific phosphine at **1**. Second order rate constants are 33.1 ± 3, 48 ± 7 and 66 ± 5 dm^3 mol^{-1} s^{-1} at 298, 308 and 318 K, respectively.

Table 1 Observed exchange rate constants, k_C, for phosphine exchange at **1** in C_6D_6 at different temperatures and [Me_2PhP]

10^3 [Me_2PhP]/mol dm^{-3}	k_C/s^{-1}	T/K
2.7	0.258 ± 0.046	298.0
14.3	0.72 ± 0.18	298.0
23.5	0.935 ± 0.047	298.0
52	1.46 ± 0.20	298.0
165	5.2 ± 0.5	298.0
208	7.3 ± 0.9	298.0
21.1	1.50 ± 0.10	308.0
57	3.97 ± 0.28	308.0
145	7.6 ± 0.6	308.0
20.8	1.57 ± 0.22	318.0
144	9.7 ± 1.3	318.0

Mechanism

The rate law is second order supporting a rate-determining attack of phosphine on the complex. The activation parameters display fairly large errors but still they are by no means borderline; the entropy of activation is highly negative and the enthalpy is fairly low. Taken together this supports an associative mode of activation. In the last 15 years it has become clear that dissociative activation is a possible alternative in exchange and substitution reactions also for square planar complexes, especially organometallic ones. In all cases reported so far the complexes contain two strong σ donors in mutual *cis* positions.[2,3] In the present case we have four tertiary ligands, all of which are weaker σ donors than *e.g.* σ bonded hydrocarbyl or silyl ligands (phosphines and stannyl ligands display a similar and intermediate ground state *trans* influence).[4] It is therefore not surprising that we see the normal associative mode of activation.

Despite the four sterically demanding tertiary ligands the observed phosphine exchange rate of **1** is fairly high and of the same order as *e.g.* the exchange of dimethyl sulfide (dms) at $Pt(dms)_4^{2+}$, substitution of iodide by pyridine in $PtI_3(PPh_3)^-$ or substitution of 5-aminoquinoline (5-aquin) by PMe_2Ph in *cis*-$PtPh_2(CO)$(5-aquin).[5,7e,13] The high reactivity is probably mostly due to the *trans* effect of the phosphine ligands. Unfortunately, no direct comparison of *cis* effects is possible since there are very little data available for exchange at other *trans*-$PtX_2(PR_3)_2$ complexes with less sterically hindering X ligands such as halides. It has been reported that exchange at *trans*-$PtI_2(PMe_2Ph)_2$ **2** in $CDCl_3$ gives rise to some broadening of the lines in the ^{31}P NMR spectrum at room temperature but the kinetics was not evaluated quantitatively.[8] Thus, **2** probably displays a higher reactivity than **1**, but it is still surprising that the triphenylstannyl complex with sterically blocking ligands reacts so fast. Probably the steric hindrance of these ligands is counterbalanced by their high π acidity, an effect that will stabilise a 5-coordinate transition state electronically and decrease the activation barrier. It is known that introduction of π accepting *cis* ligands into complexes that are dissociatively activated can stabilise an associative transition state to the extent that a change to an associative mode of activation occurs.[14]

Further support for a fairly stable, closed transition state comes from the activation parameters. Recently Elding and co-workers used the contribution of $T\Delta S^{\ddagger}$ to $\Delta G^{\ddagger}$ as a measure of how well ordered the transition state is.[15] It seems that a high entropy contribution is associated with substitutions *trans* to ligands which derive their *trans* effect mainly from π acidity. Thus, substitution *trans* to ethene in Zeise's anion has an entropy contribution at room temperature of around 75%,[15] similar to what is observed for substitution *trans* to triphenylstibine.[5] These substitutions are proposed to proceed with fairly closed transition states. Similar trends can be observed when comparing reactions in different steric environments; the entropy contribution goes down when the steric encumbrance goes up *e.g.* in substitution in *trans*-$Pt(PEt_3)_2(Aryl)Cl$ and *trans*-$Pt(Ph)Cl(SR_2)_2$, again suggesting that a high entropy contribution corresponds to a closed transition state.[16] In the present reaction the entropy term is responsible for around 60% of the activation barrier at room temperature and in line with the above reasoning this speaks in favour of a substantial electronic stabilisation of the transition state. Needless to say, validation of this hypothesis will require more investigations preferably of a series of closely related *trans*-bis(phosphine) complexes.

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References and notes

1 (*a*) C. H. Langford and H. B. Gray, *Ligand Substitution Processes*, W. A. Benjamin Inc., New York, 1965; (*b*) R. G. Wilkins, *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd edn., VCH Verlagsgesellschaft mbH, Weinheim, 1991, ch. 4; (*c*) R. J. Cross, *Adv. Inorg. Chem.*, 1989, **34**, 219.

2 S. Lanza, D. Minniti, P. Moore, J. Sachinidis, R. Romeo and M. L. Tobe, *Inorg. Chem.*, 1984, **23**, 4428; D. Minniti, G. Alibrandi, M. L. Tobe and R. Romeo, *Inorg. Chem.*, 1987, **26**, 3956; U. Frey, L. Helm, A. E. Merbach and R. Romeo, *J. Am. Chem. Soc.*, 1989, **111**, 8161; R. Romeo, *Comments Inorg. Chem.*, 1990, **11**, 21; D. Minniti, *J. Chem. Soc., Dalton Trans.*, 1993, 1343.

3 O. F. Wendt, R. J. Deeth and L. I. Elding, *Inorg. Chem.*, 2000, **39**, 5271.

4 O. F. Wendt, Ph.D. Thesis, Lund University, 1997.

5 O. F. Wendt and L. I. Elding, *J. Chem. Soc., Dalton Trans.*, 1997, 4725.

6 R. V. Lindsey, Jr., G. W. Parshall and U. G. Stolberg, *J. Am. Chem. Soc.*, 1965, **87**, 658.

7 (*a*) Ö. Gröning, T. Drakenberg and L. I. Elding, *Inorg. Chem.*, 1982, **21**, 1820; (*b*) J. J. Pesek and W. R. Mason, *Inorg. Chem.*, 1983, **22**, 2958; (*c*) L. Helm, L. I. Elding and A. E. Merbach, *Inorg. Chem.*, 1985, **24**, 1719; (*d*) Y. Ducommun, L. Helm, A. E. Merbach, B. Hellquist and L. I. Elding, *Inorg. Chem.*, 1989, **28**, 377; (*e*) U. Frey, S. Elmroth, B. Moullet, L. I. Elding and A. E. Merbach, *Inorg. Chem.*, 1991, **30**, 5033; (*f*) N. Hallinan, V. Besançon, M. Forster, G. Elbaze, Y. Ducommun and A. E. Merbach, *Inorg. Chem.*, 1991, **30**, 1112; (*g*) O. F. Wendt and L. I. Elding, *J. Chem. Soc., Dalton Trans.*, 1997, 4733.

8 D. G. Cooper and J. Powell, *J. Am. Chem. Soc.*, 1973, **95**, 1102.

9 C. Eaborn, A. Pidcock and B. R. Steele, *J. Chem. Soc., Dalton Trans.*, 1975, 809.

10 G. A. Morris and R. Freeman, *J. Magn. Reson.*, 1978, **29**, 433.

11 J. J. Led and H. Gesmar, *J. Magn. Reson.*, 1982, **49**, 444.

12 A. R. Curtis and W. P. Sweetenham, *FACSIMILE/CHEKMAT User's manual*, Harwell Laboratory, 1988.

13 R. Romeo, G. Arena and L. Monsù Scolaro, *Inorg. Chem.*, 1992, **31**, 4879.

14 R. Romeo, A. Grassi and L. Monsù Scolaro, *Inorg. Chem.*, 1992, **31**, 4383.

15 M. R. Plutino, S. Otto, A. Roodt and L. I. Elding, *Inorg. Chem.*, 1999, **38**, 1233.

16 G. Faraone, V. Ricevuto, R. Romeo and M Trozzi, *J. Chem. Soc., Dalton Trans.*, 1974, 1377; O. F. Wendt, Å. Oskarsson, J. G. Leipoldt and L. I. Elding, *Inorg. Chem.*, 1997, **36**, 4514.

17 A. D. Bain and J. A. Cramer, *J. Magn. Reson.*, 1996, **118A**, 21.