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On the Reaction of Carbon Monoxide with the Complexes *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4PPh_3(H_2O)]^{2+}$

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Abstract

The complex *trans*-$[Ru(NH_3)_4P(OEt)_3CO](PF_6)_2$ has been isolated and characterized by micro-analysis, electronic, vibrational and voltammetric spectra and conductometric measurements. The aquation of the coordinated CO ligand has been studied. k_1, k_{-1} and K_{eq} for the reaction

$$trans\text{-}[Ru(NH_3)_4P(OEt)_3(H_2O]^{2+} + CO \rightleftharpoons trans\text{-}[Ru(NH_3)_4P(OEt)_3CO]^{2+} + H_2O$$

are 3.11 $M^{-1}\ s^{-1}$, $2.6 \times 10^{-5}\ s^{-1}$ and $1.2 \times 10^5\ M^{-1}$ at 25 °C, $\mu = 0.10$ in $NaCF_3CO_2$, pH = 3.0, respectively.

Attempts to prepare *trans*-$[Ru(NH_3)_4PPh_3CO]^{2+}$ are described.

Introduction

Phosphanes, despite being well known for a long time as ligands in homogeneous catalysis, have not been studied with respect to their *trans*-influence and *trans*-effect for a well defined octahedral environment. Taking as models complexes of the type *trans*-$[Ru(NH_3)_5(H_2O)L]^{3+/2+}$, where L = phosphane, we are developing in our laboratory a systematic approach towards understanding the chemical [1–3] behavior of phosphanes as ligands.

In the course of our investigation on ruthenium–phosphorous complexes, and their ability to activate small molecules, we report some results on the carbonyl derivative.

Experimental

Most starting materials were purchased from Aldrich and were used as supplied. Isonicotinamide, isn, was purified by recrystallization [1]. When dealing with ruthenium(II) complexes, all the manipulations were carried out under argon. The argon, 99.9% (White Martins S/A) was purified using $Cr(ClO_4)_2$ solutions and zinc amalgam. The carbon monoxide, 99.9% (White Martins S/A) was purified using alkaline pyrogallol solutions. Alternatively CO was generated using the reaction between formic acid and sulfuric acid. The electrochemical measurements were performed on a PARC system Model 173 Potentiostat/Galvanostat, a model 175 Universal Programmer and a RE 0074 X-Y Recorder. The conductometric measurements were performed on a Micronal Conductometer B331 with a cell constant $\theta = 0.786\ cm^{-1}$. The cell for cyclic voltammetric measurements employed carbon paste, vitreous carbon or platinum as the working electrode and S.C.E. as the reference electrode. For the electrochemical and kinetic experiments the temperature was kept constant using a Superohm thermostat. The infrared spectra of the complex in KBr or Nujol films were obtained using a Perkin-Elmer 700 A spectrophotometer. The UV–Vis spectra were recorded on a Varian Techtron Model 636 M spectrophotometer. $RuCl_3 \cdot xH_2O$, purchased from Mattey Bishop, was used as the starting material for the synthesis of ruthenium complexes. The complexes $Ru(NH_3)_5Cl_3$, $[Ru(NH_3)_5(H_2O)](PF_6)_2$, *trans*-$\{Ru(NH_3)_4[P(OEt)_3]_2\}(PF_6)_2$ and *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](PF_6)_2$ were prepared as described in the literature [1].

Synthesis of trans-$[Ru(NH_3)_4P(OEt)_3CO](PF_6)_2$

In a typical experiment, about 0.2 g of the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](PF_6)_2$ complex was dissolved in 2–3 ml of degassed 0.10 M CF_3COOH. Solutions of the Ru(II) complex were protected from light and oxygen and kept in a CO flow for 5–6 h at room temperature at 1 atm. The complex *trans*-$[Ru(NH_3)_4P(OEt)_3CO](PF_6)_2$ was precipitated by adding 0.3 g of solid $(NH_4)PF_6$. *Anal.* Calc.: C, 12.90; H, 4.15; N, 8.62. Found: C, 12.75; H, 4.30; N, 8.72%. The yield was better than 80%.

Kinetic Measurements

Aqueous isonicotinamide 0.6 M solutions with the pH and ionic strength previously adjusted were degassed for 25–35 min in a flash immersed in a constant temperature bath. After the deaeration, a

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weighted sample of carbonyl–phosphite complex was added. The solution was transferred to the spectrophotometric cell (previously flushed with argon) through teflon tubing and the reaction followed by measuring [1] the change in absorbance at 360 nm. The rate constants were determined graphically from a plot of $\log(A_\infty - A_t)$ *versus* time. Straight lines were obtained for at least three half-lives. The rate constant data calculated through this procedure and by Guggenhein's method [4, 5] agree quite well. The formation of carbonyl complexes was considered to take place according to the equation:

$$\textit{trans}\text{-}[\mathrm{Ru(NH_3)_4P(OEt)_3(H_2O)}]^{2+} + \mathrm{CO} \xrightleftharpoons{k_{\mathrm{obs}}} \textit{trans}\text{-}[\mathrm{Ru(NH_3)_4P(OEt)_3CO}]^{2+} + \mathrm{H_2O} \qquad (1)$$

The reaction was followed by measuring the change in absorbance at $\lambda = 320$ nm. An isosbestic point was observed at 296 nm and persisted for at least three half-lives. Kinetic runs were carried out under pseudo first order conditions, (excess of CO).

Plots of $\log(A_\infty - A_t)$ *versus* time are linear for at least three half-lives. The solubility of CO in water at 25 °C is given as 8.7×10^{-4} M [6].

The stated experimental values are the mean of at least three independent determinations whose agreement was better than 94%.

Results and Discussion

From the reaction of *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3(H_2O)}]^{2+}$ with CO in aqueous solutions, it was possible to isolate a white solid which, when analysed, was shown to be *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3CO}](\mathrm{PF_6})_2$.

Conductometric measurements in nitromethane (at 25 °C) for the complexes *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3CO}](\mathrm{PF_6})_2$ and *trans*-$\{\mathrm{Ru(NH_3)_4[P(OEt)_3]_2}\}(\mathrm{PF_6})_2$ yield $\Delta = 101.0$ mol^{-1} cm^{+2} ohm^{-1} and 103.8 mol^{-1} cm^{+2} ohm^{-1}, respectively. As the bisphosphite complex *trans*-$\{\mathrm{Ru(NH_3)_4[P(OEt)_3]_2}\}(\mathrm{PF_6})_2$ is a well established 1:2 electrolyte [1, 2], we assigned a monomeric structure to the carbonyl derivative.

The UV spectrum of the carbonyl–phosphite complex in aqueous solution shows an absorption maximum at $\lambda = 284$ nm, $\epsilon = (4.7 \pm 0.2) \times 10^2$ M^{-1} cm^{-1}, due to a d–d transition.

The voltammetric spectra for the carbonyl–phosphite complex ion *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3CO}]^{2+}$ exhibit only the anodic peak ($E_{\mathrm{pa}} = (1.11 \pm 0.02)$ V *versus* S.C.E., $\mu = 0.10$ in $\mathrm{NaCF_3CO_2}$ and 1.0×10^{-3} M $\mathrm{CF_3COOH}$ at 25 °C).

Exhaustive controlled-potential electrolysis at $E_{\mathrm{pa}} = +1.3$ *versus* S.C.E., or the oxidation of *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3CO}]^{2+}$ with $\mathrm{Ce^{4+}}$ in aqueous solutions yields *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3(H_2O)}]^{3+}$ as the product. From the number of Faradays or equivalents of $\mathrm{Ce^{4+}}$ per mol of monophosphite complex for the overall reaction, the following scheme can be proposed:

$$\textit{trans}\text{-}[\mathrm{Ru(NH_3)_4P(OEt)_3CO}]^{2+} + \mathrm{H_2O} \xrightarrow{-3e^-} \textit{trans}\text{-}[\mathrm{Ru(NH_3)_4P(OEt)_3(H_2O)}]^{3+} + \mathrm{CO_2} \qquad (2)$$

A similar behavior has been described [7–9] for the $[\mathrm{Ru(NH_3)_5CO}]^{2+}$ complex.

No experimental evidence for the dehydratation of formic acid by the *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3(H_2O)}]^{3+}$ complex has been obtained. Solutions of the complex *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3(H_2O)}]^{3+}$ in $\mathrm{HCOOH/HCOO^-}$ buffers show only the reduction Ru(III)–Ru(II). Probably an intermediate type *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3OCOH}]^{2+}$, (analogous to that proposed for the $[\mathrm{Ru(NH_3)_5H_2O}]^{3+}$ system [ref. 12 in our ref. 8], will be quite unstable due to internal electron transfer process yielding $\mathrm{CO_2}$.

The vibrational spectrum of the *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3CO}]^{2+}$ complex shows an absorption at 1995 cm^{-1} ascribed to ν(CO) frequency and is about 110 cm^{-1} lower than that observed for free CO(ν(CO) = 2100 cm^{-1}) [10], and not very far from that for $[\mathrm{Ru(NH_3)_5CO}]\mathrm{I_2}$ (ν(CO) = 1955 cm^{-1}) and $[\mathrm{Ru(NH_3)_5CO}]\mathrm{Cl_2}$ (ν(CO) = 1930–1916 cm^{-1}) [11–13].

It is generally accepted that the back-bonding in metal carbonyl complexes weakens the C–O bond (the effect being noticed by a decrease in ν(CO)). The σ bonding will affect the ν(CO) value in the opposite direction since the lone pair in CO is weakly antibonding for C and O. Considerable back-bonding between Ru(II) and CO is observed in the *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3CO}](\mathrm{PF_6})_2$ complex, and is also supported by our electrochemical results.

The oxidation of *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3CO}]^{2+}$ to the corresponding Ru(III) complex is observed at potentials 600 mV more positive with respect to the *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3(H_2O)}]^{2+}$ ion. This is indicative of a strong stabilization of Ru(II) with respect to Ru(III) in the monophosphite complex. The shifts in the E_{pa} potentials for the complexes *trans*-$[\mathrm{Ru(NH_3)_4P(OEt)_3CO}]^{2+}$ and *trans*-$[\mathrm{Ru(NH_3)_5CO}]^{2+}$ relative to $[\mathrm{Ru(NH_3)_5(H_2O)}]^{2+}$ are about the same.

It is noticeable that in spite of the strong $4d_\pi$–$3d_\pi$ back-bonding interaction observed in the Ru(II)–$\mathrm{P(OEt)_3}$ system (the back-bonding stabilization energy is [14] about 8 kcal mol^{-1}), the Ru(II) center is still able to coordinate strongly to carbon monoxide.

The biphillic character of the triethyl phosphite and of the carbon monoxide molecule should be very important for such interactions. Thus, in these circumstances, a synergic effect between the σ and π components in the $\mathrm{(OEt)_3P}$–Ru–CO bonds must be operative. With molecular nitrogen and sulphur dioxide (σ donors less strong than CO) such synergism, if existent, must be weak, and may account for our inability to produce the *trans*-$[Ru(NH_3)_4P(OEt)_3N_2]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OEt)_3SO_2]^{2+}$ complex ions.

The aquation of the carbonyl derivative has been studied using isonicotinamide (isn) as scavenger:

$$\textit{trans}\text{-}[Ru(NH_3)_4P(OEt)_3CO]^{2+} + H_2O \xrightarrow[\text{slow}]{k_{-1}} \textit{trans}\text{-}[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} + CO \quad (3)$$

$$\textit{trans}\text{-}[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} + \text{isn} \xrightarrow[\text{fast}]{} \textit{trans}\text{-}[Ru(NH_3)_4P(OEt)_3\text{isn}]^{2+} + H_2O \quad (4)$$

As shown in Table I, CO is released slowly from the complex (the order of the magnitude for k_{-1} is 10^{-5} s^{-1}) and the effect of the hydrogen ion concentration is weak in the 10^{-3}–10^{-13} M range.

The activation parameters are: $\Delta H^{\neq}_{-1} = 18$ kcal mol^{-1}, $\Delta S^{\neq}_{-1} = -18$ cal K^{-1} mol^{-1}. These data fit very well in an isokinetic plot for the aquation reactions of the bisphosphite complexes [2]. Since the ruthenium(II) complex is an 18 electron system and is low spin, the substitution reaction should be governed by a dissociative activation [1–3] process, an energy of about 18 kcal mol^{-1} being necessary to break the ruthenium–carbonyl bond in the *trans*-$[Ru(NH_3)_4P(OEt)_3CO]^{2+}$ complexes ion.

The *trans*-$\{Ru(NH_3)_4[P(OEt)_3]_2\}^{2+}$ complex ion yields the monophosphite complex *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ at a specific rate [1] of 1.1×10^{-5} s^{-1}. Thus, the carbon monoxide complex under the same experimental conditions undergoes aquation about three times faster than the bisphosphite complex.

TABLE I. Kinetic Data for the Reaction:

$$\textit{trans}\text{-}[Ru(NH_3)_4P(OEt)_3CO]^{2+} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{trans}\text{-}[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} + CO$$

NaOH (M)	T (°C)	C_{H^+} (M)	$C_{Ru(II)} \times 10^5$ (M)	k_{-1} [a] (s^{-1})	k_1 [b] (M^{-1} s^{-1})
	25	$10^{-3.0}$	5.0	2.6×10^{-5}	
	25	$10^{-5.5}$	5.0	3.0×10^{-5}	
	25	$10^{-9.5}$	5.0	6.8×10^{-5}	
	25	10^{-13}	5.0	8.1×10^{-5}	
0.5	25		5.0	2.4×10^{-4}	
1.0	25		5.0	8.4×10^{-3}	
	15	$10^{-5.5}$	5.0	7.7×10^{-5}	
	35	$10^{-5.5}$	5.0	8.0×10^{-5}	
	25	$10^{-3.0}$	8.0		3.15
	25	$10^{-3.0}$	10.0		3.10
	25	$10^{-3.0}$	15.0		3.07

[a] $\mu = 1.0$, NaOH–CF_3COOH, $C_{isn} = 0.60$ M. [b] $\mu = 0.10$, $NaCF_3CO_2$.

The substitution of the water molecule in *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ for CO, takes place with a second order specific rate of 3.11 M^{-1} s^{-1}, at 25 °C, $\mu = 0.10$ $NaCF_3CO_2$.

Therefore, the equilibrium quotient, k_1/k_{-1}, for the reaction:

$$\textit{trans}\text{-}[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} + CO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \textit{trans}\text{-}[Ru(NH_3)_4P(OEt)_3CO]^{2+} + H_2O \quad (5)$$

could be estimated as 1.2×10^5 M^{-1}. The values of k_1 and K_{eq} for CO as entering ligand are not so different from those determined for the substitution of $P(OEt)_3$ on the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ system, 0.75 M^{-1} s^{-1} and 6.7×10^4 M^{-1}, respectively [1].

From the changes in electronic spectra and the characteristic odour of the free phosphite molecules in strong alkaline medium, ($C_{NaOH} \geqslant 1$ M), it can be inferred that a decomposition of the carbonyl–phosphite complex also takes place. Thus we did not carry out experiments in stronger alkaline conditions.

This investigation has been extended to the *trans*-$[Ru(NH_3)_4PPh_3(H_2O)]^{2+}$ system. Despite the fact that the monophosphine complex is not very sensitive to oxygen [15], ($E^{\circ\prime} = (0.55 \pm 0.02)$ V *versus* S.C.E., $\mu = 0.10$ $NaCF_3COO$ and 1×10^{-3} M in CF_3COOH at 25 °C), the oxidation of the coordinated triphenyl phosphine molecule to phosphine oxide does occur in the presence of CO.

The triphenyl phosphine molecule in the *trans*-$[Ru(NH_3)_4PPh_3(H_2O)]^{2+}$ complex is oxidized by traces of O_2. It should be pointed out that the phosphite molecule in *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ ($E^{\circ\prime} = (0.52 \pm 0.02)$ V *versus* S.C.E., $\mu = 0.10$ $NaCF_3CO_2$, 1×10^{-3} M in CF_3COOH at 25 °C), under the same experimental conditions, does not undergo oxidation. In fact the coordinated phosphite molecule is not oxidized [1] even by Ce^{4+}, Br_2, or H_2O_2 in acidic media. We do not have at this moment a clear explanation for the triphenyl phosphine oxidation, however it seems feasible that, as observed for other systems [16] carbon monoxide can catalyse this reaction.

The solids obtained from the *trans*-$[Ru(NH_3)_4PPh_3(H_2O)]^{2+}$ and CO reaction did not analyse well, but show a strong and well defined ν(CO) band at 1931 cm^{-1}.

Although the pure compound has not been isolated, it was possible to verify the presence of *trans*-$[Ru(NH_3)_4PPh_3CO]^{2+}$ ion in solution. On standing, the *trans*-$[Ru(NH_3)_4PPh_3CO]^{2+}$ solution slowly forms both the *trans*-$[Ru(NH_3)_4PPh_3(H_2O)]^{2+}$ and *trans*-$[Ru(NH_3)_4(CO)(H_2O)]^{2+}$ species.

The presence of such complex ions is suggested by the electronic spectra obtained by adding isn to the carbonyl–phosphine complex in solution. Under these conditions the two absorption peaks (characteristic of species *trans*-$[Ru(NH_3)_4PPh_3isn]^{2+}$ [17] and *trans*-$[Ru(NH_3)_4(H_2O)isn]^{2+}$ [6]) are seen at 394 and 476 nm respectively.

These systems are currently being studied in our laboratory and the results will be reported later.

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References

1 D. W. Franco and H. Taube, *Inorg. Chem., 17,* 571 (1978), and refs. therein.

2 D. W. Franco, *Inorg. Chim. Acta, 32,* 273 (1979).

3 D. W. Franco, *Inorg. Chim. Acta, 48,* 1 (1981).

4 N. B. Chapman and J. Shoter, 'Advances in Linear Free Energy Relationships', Plenum, New York, 1972.

5 G. M. Fleck, 'Chemical Reaction Mechanism', Holt, Rinehart and Winston, New York, 1971.

6 H. E. Toma, J. M. Malin and E. Giesbrecht, *Inorg. Chem., 12,* 2084 (1973).

7 S. S. Isied and H. Taube, *Inorg. Chem., 15,* 3070 (1976).

8 J. F. Wishart, H. Taube, K. J. Breslaver and S. S. Isied, *Inorg. Chem., 23,* 2997 (1984).

9 G. D. Watt, *J. Am. Chem. Soc., 94,* 7351 (1972).

10 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley, New York, 1963.

11 C. H. Campbell, A. R. Dias, M. L. H. Green, T. Saito and M. G. Swanwick, *J. Organomet. Chem., 14,* 349 (1969).

12 J. A. Stanko and T. W. Starinshak, *Inorg. Chem., 8,* 2156 (1969).

13 A. D. Allen, T. Eliades, R. O. Harris and P. Reinslau, *J. Can. Chem., 47,* 1605 (1969).

14 R. Sernaglia and D. W. Franco, *Inorg. Chem.,* submitted for publication.

15 R. G. Pearson, *Inorg. Chem., 23,* 4675 (1984).

16 B. R. James, S. R. Milkensen, T. W. Leung, G. M. Willians and R. Wong, *Inorg. Chim. Acta, 85,* 209 (1984).

17 J. M. Rezende and D. W. Franco, *XVIII Congresso Nazionalle di Chimica Inorganica,* Como, Italy, 1985.