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Synthesis of Phosphite Complexes of Ruthenium(II)

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By reacting trans-$[Ru(NH_3)_4SO_2(H_2O)](CF_3SO_3)_2$, $[Ru(NH_3)_5(H_2O)](PF_6)_2$ *or* $[Ru(NH_3)_5(H_2O)](CF_3SO_3)_3$ *with phosphites in acetone, the complexes* trans-$[Ru(NH_3)_4(P(OR)_3)_2]X_2$ *(*$X = PF_6^-$*, or* $CF_3SO_3^-$*;* R *= methyl, isopropyl, or butyl) have been prepared. The mixed complexes* trans-$[Ru(NH_3)_4P(OEt)_4P(OR)_3](CF_3SO_3)_2$*, (*$R$ *= methyl, isopropyl, butyl, or phenyl) were isolated following reaction of* trans-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_2$ *with phosphites in acetone. The new complexes have been characterized on the basis of their microanalyses, cyclic voltammetry, conductivity, magnetic susceptibility data and vibrational and electronic spectra. All of these complexes are reasonably air stable, in accord with* $E^{\circ\prime}$ *data for the Ru(III)/Ru(II) couple of these compounds, which are in the range of +0.69 – 0.63 V. They are all diamagnetic and behave as 1:2 electrolytes in solution. Both series of complexes exhibit absorption bands at 262 nm (*$\epsilon = 510$–$410\ M^{-1}\ cm^{-1}$ *and 294 nm (*$\epsilon = 350$–$200\ M^{-1}\ cm^{-1}$*) attributable to d–d transitions.*

Introduction

The filled 3s orbital on phosphorus, suitable for σ bonding, and the existence of vacant $3d_\pi$ orbitals, available for backbonding, make phosphorus compounds very attractive as ligands [1, 3] for ruthenium(II). The synthesis and characterization of a number of Ru(II) complexes containing tertiary phosphines [4–9] have been reported. Some of these compounds exhibit interesting catalytic properties and others have been used as synthetic intermediates in Ru(II) chemistry. In contrast to phosphines, few data with regard to phosphites as ligands are available [3,10].

In this paper, the synthesis of the complexes *trans*-$[Ru(NH_3)_4P(OR_1)_3P(OR_2)_3]L_2$ ($R_1 = R_2$, or $R_1 \neq R_2$; $L = PF_6^-$ or $CF_3SO_3^-$) is described. The reaction of phosphites with $[Ru(NH_3)_5(H_2O)](PF_6)_2$, $[Ru(NH_3)_5(H_2O)](CF_3SO_3)_3$ or *trans*-$[Ru(NH_3)_4SO_2(H_2O](CF_3SO_3)_2$ in acetone seems to be a general route for the synthesis of this type of compounds.

These complexes, in which the metal ion is in a defined environment, offer the opportunity to develop a systematic approach to the understanding of the basic chemistry of phosphites as ligands [2, 3]. Since Ru(II) complexes are inert with respect to substitution reactions [2], these compounds represent an excellent model for the study of changes in the reactivity of the metal center upon coordination to phosphites, and of changes in the phosphite chemistry itself.

Another point of interest, currently under investigation in our laboratories, is the potential anticholinesterasic activity of these complexes [11], as well as their potential as sugar reagents in histochemistry [12].

Experimental Section

Chemical and Reagents

Water doubly distilled in glass was used throughout. The acetone, ether and ethanol employed for the preparations were freshly distilled before use. The phosphites (Aldrich) were purified by treatment with metallic sodium followed by vacuum distillation. Their purity was checked by infrared spectroscopy [3].

Preparations of Ruthenium Compounds

Standard preparations

The starting material $Ru(NH_3)_6Cl_3$ was purchased from Matthey Bishop, Inc. The complexes $[Ru(NH_3)_5Cl]Cl_2$, $[Ru(NH_3)_4SO_2Cl]Cl$, *trans*-$[Ru(NH_3)_4SO_2(H_2O)](CF_3SO_3)_2$, $[Ru(NH_3)_5(H_2O)](PF_6)_2$ and $[Ru(NH_3)_5(H_2O](CF_3SO_3)_3$ were prepared by standard literature methods [13–16].

Preparation of new ruthenium ammine complexes containing $P(OR)_3$ *as a ligand*

trans-$[Ru(NH_3)_4(P(OR)_3)_2](CF_3SO_3)_2$ *(where* R *= methyl, butyl, isopropyl).* About 0.2 g of *trans*-$[Ru(NH_3)_4SO_2(H_2O)](CF_3SO_3)_2$ was dissolved in 200 ml of dry deaerated acetone under argon or nitrogen. By means of a syringe, 2–4 ml of the desired degassed phosphite was introduced into the reaction flask. The solution color changed from orange to pale yellow. After 6–8 hours at 23–28 °C, the solution was filtered, when necessary, and the solvent and excess phosphite eliminated by rotoevaporation. The pale yellow complex was purified by repeated precipitation from saturated ethanol solution with peroxide-free ether (200–300 ml). Conversion of the starting *trans*-$[Ru(NH_3)_4SO_2(H_2O)](CF_3SO_3)_2$ was checked by cyclic voltammetry. When starting Ru(II) still remained, the product was dissolved in acetone and the treatment with the phosphite repeated. In the cases in which the crude solid product was dark yellow the reprecipitation procedure described above or recrystallization from acetone led to a high-purity product. The solid *trans*-$[Ru(NH_3)_4(P(OR)_3)_2](CF_3SO_3)_2$ was collected by filtration, washed with ether, dried and stored under vacuum in the dark. Yields were always better than 60%.

trans-$[Ru(NH_3)_4(P(OR)_3)_2](PF_6)_2$ *(R = methyl, isopropyl, or butyl).* The synthesis of the diphosphite complex, obtained as the hexafluorophosphate salt, can also be carried out in the following manner: 0.2 g of $[Ru(NH_3)_5(H_2O)](PF_6)_2$ was dissolved in 10 ml of dry deaerated acetone. Using a syringe, 1–15 ml of the desired deaerated phosphite was transferred to the reaction flask. After 25–30 minutes, the solvent and excess phosphite were eliminated by rotoevaporation. The diphosphite complex, a pale yellow solid, was purified by reprecipitation, dried and stored as described above. Yields were always greater than 70%. Recrystallization from acetone removed a reddish impurity which was sometimes present.

trans-$[Ru(NH_3)_4(P(OR)_3)_2](CF_3SO_3)_2$ *(R = methyl, isopropyl, or butyl).* This synthetic route takes advantage of the reducing properties of the phosphites. $[Ru(NH_3)_5(H_2O](CF_3SO_3)_3$ (0.1 g) was dissolved in 10 ml of degassed acetone. Using a syringe 3–4 ml of deaerated phosphite were transferred into the Ru(III) solution. After 30 minutes, the acetone and excess phosphite were eliminated by rotoevaporation. If a solid was obtained, it was purified as described above [1]. If a brownish oil resulted a few drops of ethanol and 4–8 ml of ether were added and the solution cooled overnight (refrigerator) to obtain crystals. Yields were better than 35%.

trans-$[Ru(NH_3)_4P(OEt)_3P(OR)_3](CF_3SO_3)_2$ *(where R = methyl, isopropyl, butyl, or phenyl).* The mixed diphosphite complexes were prepared by reacting *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O](CF_3SO_3)_2$ with the desired phosphite in acetone. Although the preparation of *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_2$ is not in itself novel [3], it is not yet a common procedure. An outline of the procedure is as follows: *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2](CF_3SO_3)_2$, (0.2 g) was added to 30 ml of 10^{-3} M degassed aqueous CF_3SO_3H. The reaction mixture was maintained under argon or nitrogen at room temperature (22–27 °C) in the dark for a 60–64 h period. After elimination of the solvent by rotoevaporation, the residue was purified by reprecipitation, dried and stored as described above. Yields were better than 90%. This material was then used to prepare the mixed diphosphite complexes by the following procedure: *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O](CF_3SO_3)_2$ (0.2 g) was dissolved in 10–15 ml of dry degassed acetone. Using a syringe, 1–2 ml of the desired phosphite were transferred to the Ru(II) solution. After 20–25 minutes, the solvent and excess phosphites were eliminated by rotoevaporation. The solid obtained was purified by reprecipitation, dried and stored as described above. In the cases in which an oil was obtained the residue was first crystallized (overnight, in a refrigerator) from 4–8 ml of ether containing a few drops of ethanol. Yields were better than 80%.

If stored under vacuum and protected from light the phosphite complexes described here do not exhibit significant decomposition over a three weeks' period as judged from their absorption spectra.

Apparatus and Techniques

Ultraviolet and visible spectra were recorded on either a Cary 14 or a Perkin-Elmer 575 spectrophotometer.

Infrared spectra of KBr pellets (1:200) were recorded on a Perkin-Elmer 621 or 475 spectrophotometer, in the 4000–600 cm^{-1} range.

Conductometric measurements were carried out on a Metrohm E 365-B conductometer. The magnetic susceptibility measurements were performed with a Model 7600 Cahn Faraday Magnetic susceptibility apparatus at room temperature (23–27 °C). The compounds $Hg[Co(CNS)_4]$ and $[Ru(NH_3)_5Cl]Cl_2$ were employed as standard and control respectively [17]. Carbon, nitrogen and ruthenium analyses, see Table I, were performed by the staff of the Stanford Microanalytical Laboratory and by the staff of the Microanalytical Laboratory of the Instituto de Química of the Universidade de São Paulo. Cyclic voltammograms were recorded on an Electroscan 30 or a P.A.R. 170 device. A carbon paste was employed as indicator electrode and S.C.E. as reference electrode. The formal potentials were measured against S.C.E. and were converted to the N.H.E. reference by adding 242 mV. The reversibility of the systems was verified by applying two criteria: a) Comparing the peak-to-peak separation with that of the $Ru(NH_3)_6^{3+/2+}$ system, known to be reversible [18]; b) Comparing

TABLE I. Analytical Data for the Ruthenium–Phosphite Complexes.

Complex	C %		H %		N %		Ru %	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
trans-$[Ru(NH_3)_4(P(OMe)_3)_2](CF_3SO_3)_2$	13.4	13.1	4.23	4.28	7.83	7.90	14.1	14.3
[a]*trans*-$[Ru(NH_3)_4(P(O^iPr)_3)_2](CF_3SO_3)_2$	27.0	27.0	6.08	6.30	6.32	6.36	11.4	11.3
trans-$[Ru(NH_3)_4(P(OBut)_3)_2](CF_3SO_3)_2$	32.2	32.3	6.82	7.02	5.78	5.78	10.4	10.5
trans-$[Ru(NH_3)_4(P(OEt)_3)P(O\phi)_3](CF_3SO_3)_2$	33.1	32.1	4.49	4.34	5.94	5.73		
trans-$[Ru(NH_3)_4P(OEt)_3P(OMe)_3](CF_3SO_3)_2$	17.4	16.8	4.79	4.36	7.40	7.08		
[a]*trans*-$[Ru(NH_3)_4P(OEt)_3P(O^iPr)_3](CF_3SO_3)_2$	24.2	24.1	5.75	5.69	6.65	6.41	12.0	11.0
trans-$[Ru(NH_3)_4P(OEt)_3P(OBut)_3](CF_3SO_3)_2$	27.2	26.5	6.16	6.02	6.34	6.02		
trans-$[Ru(NH_3)_4(P(OMe)_3)_2](PF_6)_2$	10.2	10.3	4.27	4.17	7.92	7.84	14.3	14.2
[a]*trans*-$[Ru(NH_3)_4(P(O^iPr)_3)_2](PF_6)_2$	24.7	25.1	6.22	6.30	6.40	6.35		
trans-$[Ru(NH_3)_4(P(OBut)_3)_2](PF_6)_2$	30.0	31.0	6.93	7.03	5.84	5.80		

[a] O^iPr = isopropyl phosphite.

the ratio of the peak current for the cathodic relative to that for the anodic process [19].

Results and Discussion

All attempts to obtain the monophosphite complexes, *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]X_2$, by reacting equimolar amounts of phosphites and Ru(II) complexes failed. In all of these experiments, the product was a mixture of the corresponding biphosphite complex and the unreacted Ru(II) starting compound, easily identified through cyclic voltammetry. Species containing more than two coordinated phosphites were not identified, even in the presence of a fifty-fold excess of phosphite. This fact suggests, as observed when sulphite is a ligand [15, 20], a delabilizing effect upon the coordinated *cis* NH_3 ligand. The complexes containing two like phosphite ligands were identical, as judged by microanalyses, i.r., u.v. and c.v. data, independent of the starting Ru(II) complex.

The synthetic uses [14, 15] of *trans*-$[Ru(NH_3)_4SO_2(H_2O)]X_2$, the similarity of the phosphites to sulphite as a ligand, and the labilization of a single position in the coordination sphere when phosphite is present, strongly suggest the *trans* rather than *cis* structure for the title complexes.

It is known that phosphites are good *trans*-labilizing agents. In a previous study of the $P(OEt)_3$–Ru(II) system [3], we demonstrated that the second phosphite molecule substitutes at a rate of 0.75 M^{-1} sec^{-1} at 25 °C. The first phosphite should react at a slower rate than the second as judged from the product of the synthesis.

Since the basicity and structure of the phosphite ligands dealt with in this study would not be expected to change drastically, k_1 should lie in the range of 0.75–2 × 10^{-3} M^{-1} sec^{-1} and be the rate determining step in these reactions [3]. Although no direct kinetic observations have been made on the present systems, from the experience accumulated in the $P(OEt)_3$ study [3] and the synthesis, the following scheme may be suggested:

$$\left.\begin{array}{c} trans\text{-}[Ru(NH_3)_4SO_2(H_2O)]^{2+}\\ \text{or}\\ [Ru(NH_3)_5(H_2O)]^{2+}\end{array}\right\} + P(OR)_3 \underset{k_{-1}}{\overset{K_1}{\overset{k_1}{\rightleftharpoons}}} trans\text{-}[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$$

$$trans\text{-}[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+} + P(OR)_3 \underset{k_{-2}}{\overset{K_2}{\overset{k_2}{\rightleftharpoons}}} trans\text{-}[Ru(NH_3)_4(P(OR)_3)_2]^{2+}$$

where $k_1 < k_2, k_{-2} \gg k_{-1}$ and $K_1 \gg K_2$.

This supposition above is also supported by the fact that aquation in *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ takes place at a slower rate than in *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ ion [3].

When $[Ru(NH_3)_5(H_2O)]^{3+}$ is employed as reactant a reduction to Ru(II) by the phosphite

TABLE II. Banda Maxima, Molar Absorptivity[a] and Formal Reduction Potentials for Ruthenium–Phosphite Complexes.

Complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	$E^{o'}$ (V *vs.* N.H.E.)
trans-$[Ru(NH_3)_4(P(OBut)_3)_2]^{2+}$	294	$2.3 \pm 0.3 \times 10^2$	0.87 ± 0.03
	262	$4.1 \pm 0.3 \times 10^2$	
trans-$\{Ru(NH_3)_4(P(O^iPr_3)_2]^{2+}$	294	$3.1 \pm 0.3 \times 10^2$	0.87 ± 0.01
	262	$4.8 \pm 0.3 \times 10^2$	
trans-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+b}$	294	$2.4 \pm 0.2 \times 10^2$	0.89 ± 0.01
	262	$4.4 \pm 0.2 \times 10^2$	
trans-$\{Ru(NH_3)_4(P(OMe)_3)_2]^{2+}$	294	$3.5 \pm 0.3 \times 10^2$	0.92 ± 0.01
	262	$5.1 \pm 0.3 \times 10^2$	
trans-$[Ru(NH_3)_4P(OEt)_3P(OBut)_3]^{2+}$	294	$2.6 \pm 0.3 \times 10^2$	0.89 ± 0.03
	262	$4.6 \pm 0.3 \times 10^2$	
trans-$[Ru(NH_3)_4P(OEt)_3P(O^iPr)_3]^{2+}$	294	$2.8 \pm 0.3 \times 10^2$	0.87 ± 0.01
	262	$5.0 \pm 0.3 \times 10^2$	
trans-$\{Ru(NH_3)_4P(OEt)_3P(OMe)_3]^{2+}$	294	$2.7 \pm 0.3 \times 10^2$	0.92 ± 0.01
	262	$4.7 \pm 0.3 \times 10^2$	
trans-$\{Ru(NH_3)_4P(OEt)_3P(O\phi)_3]^{2+c}$	294	$2.0 \pm 0.4 \times 10^2$	0.92 ± 0.03

[a] $\mu = 0.10$ ($NaCF_3COO$, CF_3COOH), $C_{H^+} = 1.0 \times 10^{-3}$ *M*, t = 25 ± 0.2 °C. [b] Ref. 3. [c] The $P(O\phi)_3$ molecule exhibits absorption bands below 285 nm.

should precede the substitution. Upon addition of phosphites to a $[Ru(NH_3)_5(H_2O)](CF_3SO_3)_3$ solution, a yellow color, which starts to fade within a few minutes, is observed. When $[Ru(NH_3)_6](CF_3SO_3)_3$ is employed instead of the aquo complex, the yellow color persists. Since the Ru(III) complexes are known to be inert to substitution, this suggests that the Ru(III)–$P(OR)_3$ electron transfer occurs via an outer-sphere mechanism.

The complexes described here behave as 1:2 electrolytes in aqueous solution, as inferred from conductivity data. All are diamagnetic (magnetic moment < 0.54 B.M.) as expected for octahedral complexes of Ru(II).

Table II summarizes spectral data and the formal potential for the Ru(III)/Ru(II) couple of the complexes prepared in this study. With the exception of *trans*-$[Ru(NH_3)_4(P(OBut)_3)_2]^{2+}$, *trans*-$[Ru(NH_3)_4P(OEt)_3P(OBut)_3]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OEt)_3P(O\phi)_3]^{2+}$, whose c.v. present evidence for adsorption processes, all the other complexes exhibit reversible electrochemical behavior.

Many authors have pointed out the importance of the $E^{o'}$ value for the Ru(III)/Ru(II) couple in complexes where π acids are coordinated to the metal center [21–23]. Since π-bonding has been demonstrated to be important for Ru(II), but not for a Ru(III) center, the $E^{o'}$ may be employed to evaluate the extent of Ru(II) → L back-bonding in such compounds. Thus, the more positive $E^{o'}$ for the Ru(III)/Ru(II) couple, more extensive the contribution of backdonation to the stabilization of Ru(II) relative to Ru(III). Although the differences among the $E^{o'}$ values of the complexes in Table II are quite small, a trend can be noted, the formal potentials of the Ru(III)/Ru(II) couple becoming less positive as the electron-donating ability of R increases. In this way, as the electron density on phosphorus is increased, the phosphite becomes a better σ-base but a poorer π-acid.

Comparing the potential data of Table II with $E^{o'}$ for the *trans*-$[Ru(NH_3)_4(H_2O)_2]^{3+/2+}$ couple [21] it can be concluded that a stabilization of more than 0.80 V occurs upon coordination of Ru(II) to phosphites, showing that the phosphites have a higher affinity for Ru(II) than most of the ligands studied to date [2, 3]. Since phosphites are also good σ-bases and Ru(III) is a stronger σ-acid than Ru(II), the stabilization of the latter should be higher than that inferred from the E^o data. Indeed mutual strengthening of σ and π components on the Ru–$P(OR)_3$ bond should occur.

All of the complexes isolated are pale yellow solids. The solution spectra of all of the biphosphite complexes contain two weak bands in the near u.v. with maxima at 294 and 262 nm, (see Table II). Although these complexes should have D_{4h} symmetry the d–d transitions, formally forbidden, are expected to be present due to vibronic coupling [24]. Moreover, the positions of these bands are not sensitive to the nature of R or to the reducing ability of the Ru(II) center, consistent with a d–d transition. The similar nature of the spectra when $R_1 \neq R_2$ is easily explained on the basis of the similar microsymmetry in both series of compounds. We tentatively [25] assign the bands at 294 and 260 nm to

$^1A_{1g} \rightarrow {}^1A_{2g}$, ^1E_g and $^1A_{1g} \rightarrow {}^1B_{2g}$, ^1E_g transitions, respectively.

The I.R. spectra of the title complexes in the 4000–600 cm^{-1} range are the sum of the bands present in the phosphite and the ruthenium ammine moieties [26, 27]. Since the Ru–P band should appear below 350 cm^{-1}, these diphosphito complexes are now being converted from the PF_6^- or $CF_3SO_3^-$ salts to the iodide form in order to verify the presence of this band.

Further studies of the *trans*-influence, *trans*-effect and reactivity of Ru(II) coordinated phosphites are currently in progress.

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