Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Triethyl Phosphite as a Ligand on Ruthenium(II)

DOUGLAS W. FRANCO and HENRY TAUBE*

Received August 15, 1977

The reaction of $P(OEt)_3$ with $[Ru(NH_3)_5(H_2O)]^{2+}$ in acetone produces $[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ from which $[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ can be prepared by aquation in acidic solution. The aquation reaction takes place with a specific rate of $1.12 \times 10^{-5}\ s^{-1}$ at 25 °C, $\mu = 0.10$, and $[H^+] = 10^{-1}$–10^{-5} M. The compounds containing the ions are pale yellow, soluble in acetone, sparingly soluble in ethanol, and insoluble in ether. Since E_f(Ru(III)/Ru(II)) for the diphosphite and monophosphite complexes are respectively 0.88 ± 0.01 and 0.70 ± 0.01 V vs. NHE, these substances are reasonably air stable. The following derivatives have been isolated and characterized: *trans*-$[Ru(NH_3)_4P(OEt)_3(L)](PF_6)_2$, where L = isonicotinamide (isn), pyrazine (pyr), and imidazole (imN). Substitutions on the monophosphite complex have been investigated using isonicotinamide, imidazole, pyrazine, triethyl phosphite, methylpyrazinium ion ($Mepyr^+$), and sulfite ion as entering groups. The second-order specific rates are in the $7.5 \times 10^{-1}\ M^{-1}\ s^{-1}$ ($L = P(OEt)_3$)–$6.1 \times 10^{2}\ M^{-1}\ s^{-1}$ ($L = SO_3^{2-}$) range. Bond making by the entering groups in the activated complexes for substitution appears to be substantial for SO_3^{2-} and imN but not for isn, pyr, and $Mepyr^+$. In the latter cases there is noticeable outer-sphere complex formation with the entering ligand. The experimental data indicate the following order for the affinity of the monophosphite complex ion for the entering ligand: $SO_3^{2-} \approx P(OEt)_3 > imN > isn > pyr > Mepyr^+$. The position of $P(OEt)_3$ in the series of ligands arranged in order of increasing trans-labilizing effect in *trans*-$[Ru(NH_3)_4L(H_2O)]^{2+}$, measured as the second-order specific rate of the replacement of water by isn, is N_2, CO < isn < py < imN < NH_3 < OH^- < $P(OEt)_3$ < CN^- < SO_3^{2-} < imC.

Introduction

The complexes of platinum transition metals with coordinated phosphorus ligands have been known for a long time.[1,2] A considerable amount of information is available regarding syntheses and reactivity of phosphine complexes, mainly with platinum.[1-4] Though the alkyl phosphites are in some respects more tractable than the corresponding phosphines, little systematic work has been done with phosphite complexes[1-5] devoted to trying to understand their ligand qualities. The existence of vacant $3d\pi$ orbitals on the phosphorus atom makes possible back-bonding with filled $d\pi$ orbitals of metal ions, and the filled 3s orbital of phosphorus is suitable for σ bonding thus rendering it biphilic in character.[5,6]

In contrast to the situation for the square-planar systems, little information is available on the reactivity of substitution-inert divalent octahedral metal centers ligated to phosphorus.[4,7] This research was undertaken as part of a systematic study directed to understanding the basic chemistry of the phosphorus compounds as ligands in a normal octahedral environment.[8] An important aspect of the subject is to explore the changes in chemical properties induced on the Ru(II) center by attaching to it one or more phosphorus ligands. The data on the Ru(II)–P systems are not numerous and many pertain to complexes in which the metal ion is surrounded by diverse ligands, making it difficult to establish correlations.[2,3,9-11] The ruthenium(II) ammines readily lend themselves to a systematic exploration of the effects of the ligand of interest on the lability of the Ru(II)–H_2O bonds and on the affinity of the metal center for other ligands,[12] and data of this kind obtained for the phosphite complexes can be expected to improve our understanding of the nature of phosphites as ligands.

An additional incentive for undertaking the studies was the consideration that sulfite ion by labilizing a ligand on Ru(II) trans to it and by being subject to removal by oxidation has proven to be useful for preparative purposes.[13,14] There are limitations to its use, however, and it was hoped that phosphite in taking the place of sulfite might have advantages in certain circumstances. This hope, we hasten to add, has not been realized except insofar as the phosphite complexes themselves are the focus of interest.

Experimental Section

1. Chemicals and Reagents. (a) Ligands. Pyrazine (pyr), puriss grade 99%+ (Aldrich), was used as supplied. Imidazole (imN) (Aldrich) and isonicotinamide (isn) (Aldrich) were purified by recrystallization from benzene and water, respectively. Methylpyrazinium ($Mepyr^+$) *p*-toluenesulfonate was prepared by a method outlined by Magnuson.[15] Triethyl phosphite, $P(OEt)_3$ (Aldrich), was purified by distillation under metallic sodium as described in the literature.[16] The purity of the phosphite was monitored by IR spectra. The absence of the bands at 2350–2440 cm^{-1} (P–H) and 1260–1270 cm^{-1} (P=O) was taken as proof of absence of diethyl phosphite in the sample.[17]

Unless otherwise mentioned, all other chemicals were of analytical purity and used as supplied.

(b) Ruthenium Complexes (Standard Preparations). $[Ru(NH_3)_5Cl]Cl_2$,[18] *trans*-$[Ru(NH_3)_4(SO_2)Cl]$,[19] $[Ru(NH_3)_5(H_2O)](PF_6)_2$,[20] and $[Ru(NH_3)_5(H_2O)](CF_3SO_3)_3$[21] were prepared as described in the literature.

(c) Preparation of New Ruthenium Ammines with Triethyl Phosphite as Ligand. *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2](PF_6)_2$. One- or two-tenths of a gram of $[Ru(NH_3)_5(H_2O)](PF_6)_2$ was added to 10 mL of previously deaerated dry acetone, under an argon atmosphere. Using the syringe technique, 1 mL of triethyl phosphite, already deaerated, was transferred to the reaction flask (these operations should be done in the hood), whereupon the orange color of the Ru(II) solution was discharged. Sometimes a pink color appeared, the cause of which was not discovered. After 25–30 min at room temperature (22–27 °C), the solvent and the excess of phosphite were eliminated by rotoevaporation. A light yellow solid was obtained. It was sparingly soluble in ethanol and water and insoluble in ether. The solid was dissolved in the minimum amount of acetone and reprecipitated by adding 100–150 mL of peroxide-free ether, then filtered and washed with ether, and finally dried and stored under vacuum while protected from light. When a reddish impurity was also produced, it was eliminated by recrystallizing the product from acetone or by washing the solid with distilled water. The yield was better than 70%. Anal. Calcd for $[Ru(NH_3)_4(P(OEt)_3)_2](PF_6)_2$: C, 18.2; H, 5.31; N, 7.08; Ru, 12.8; F, 28.8. Found: C, 18.1; H, 5.24; N, 7.04; Ru: 12.9; F, 28.2.

trans-$[Ru(NH_3)_4(P(OEt)_3)_2](CF_3SO_3)_2$. Another route to the diphosphite complex was devised. The solid *trans*-$[Ru(NH_3)_4(SO_2)(H_2O)](CF_3SO_3)_2$ (0.1–0.2 g) was added to 200 mL of deaerated dry acetone under argon. Using syringes, 2–3 mL of degassed triethyl phosphite was transferred to the reaction flask. The original orange color of the Ru(II) solution began slowly to fade. Sometimes a precipitate formed, which has been identified by microanalysis as a mixture of $[Ru(NH_3)_4(SO_2)Cl]Cl$ and $[Ru(NH_3)_4(SO_2)Cl]CF_3SO_3$ produced because of contamination of the starting material by the chloro complex. After 4–6 h at room temperature and under argon, the solution was filtered, when necessary, and the solvent and the excess of phosphite were eliminated by rotoevaporation. The solid was dissolved in the minimum amount of absolute ethanol and reprecipitated by adding 200–300 mL of peroxide-free ether. The compound

0020-1669/78/1317-0571$01.00/0 © 1978 American Chemical Society

was filtered and washed thoroughly with ether. When the solid was deep yellow, the reprecipitation procedure was repeated. The product was substantially more soluble in water and ethanol than the corresponding hexafluorophosphate salt. It was dried in a desiccator and stored, protected from light, under vacuum. The yield was better than 80%. Anal. Calcd for $[Ru(NH_3)_4(P(OEt)_3)_2](CF_3SO_3)_2$: C, 20.9; H, 5.22; N, 6.9; Ru, 13.0; F, 14.2. Found: C, 20.8; H, 5.17; N, 7.08; Ru, 12.3; F, 14.1.

Since the ligand is a reducing agent,[5,6] the title compound could also be obtained by the reaction of triethyl phosphite with $[Ru(NH_3)_5(H_2O)](CF_3SO_3)_3$ in acetone. After evaporating the solvent and the excess of triethyl phosphite, a brownish oil resulted. On adding a few drops of ethanol and 4–6 mL of ether to this oil and cooling overnight in a refrigerator, the compound crystallized. The yield was better than 35%. Anal. Found: C, 21.0; H, 5.27; N, 6.97; Ru, 12.7; F, 14.2. No significant decomposition of the diphosphite compounds was observed within 1 month, using the absorption spectrum as indicator of purity.

***trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_2$.** Two-tenths of a gram of *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2](CF_3SO_3)_2$ was added to 20–25 mL of degassed 10^{-3} M trifluoromethanesulfonic acid. The reaction flask was kept protected from light, under argon and at room temperature (22–27 °C), for a period of ~60 h. The solvent was eliminated by rotoevaporation. The residue was dissolved in the minimum amount of absolute ethanol (1–2 mL) and precipitated by adding ether (200–300 mL) free of peroxides. The solid was collected by filtration, washed with ether, and dried under vacuum. It was stored under vacuum and protected from light. No significant decomposition was found to occur over a 2-week period, as judged by the absorption spectrum. Anal. Calcd for $[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_2$: C, 14.7; H, 4.49; N, 8.60; Ru, 15.1; P, 4.84; S, 9.84. Found: C, 15.2; H, 4.35; N, 8.68; Ru, 15.5; P, 4.76; S, 10.4.

***trans*-$[Ru(NH_3)_4P(OEt)_3(L)](PF_6)_2$ (L = isn, imN, pz).** One-tenth of a gram of *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_2$ was dissolved in 1 mL of water. In another flask a solution saturated in L and in NH_4PF_6 was prepared. Equal volumes of the solutions were mixed while stirring. The precipitation was immediate. The isn derivative was orange, the pyr derivative deep orange, and the imN derivative white. The solution was allowed to cool in the refrigerator for 0.5 h to improve the yield, which was better than 60%. The precipitates were filtered, washed with ether, and then dried and stored in a vacuum desiccator protected from light. The solids showed no signs of decomposition, as judged by their spectra, over a period of 3 weeks. Anal. Calcd for $[Ru(NH_3)_4P(OEt)_3(isn)](PF_6)_2$: C, 19.3; H, 4.42; N, 11.2; Ru, 13.5. Found: C, 19.0; H, 4.36; N, 11.1; Ru, 13.3. Calcd for $[Ru(NH_3)_4P(OEt)_3(pyr)](PF_6)_2$: C, 17.0; H, 4.39; N, 11.9; Ru, 14.3. Found: C, 16.5; H, 4.36; N, 11.9; Ru, 14.3. Calcd for $[Ru(NH_3)_4P(OEt)_3(imN)](PF_6)_2$: C, 15.6; H, 4.47; N, 12.1; Ru, 14.6. Found: C, 15.5; H, 4.52; N, 11.8; Ru, 14.5.

Microanalyses were performed by the staff of the Stanford Microanalytical Laboratory.

2. Apparatus and Methods. (a) Ultraviolet and visible spectra were recorded on a Cary 15, Cary 14, or Beckman Acta MVII recording spectrophotometer.

(b) The infrared spectra were recorded on a Perkin-Elmer 621 grating spectrophotometer covering the region 4000–250 cm^{-1}.

(c) Cyclic voltammograms were obtained employing an electrochemical apparatus designed and constructed by G. Tom.[22] The following cell was employed for the CV measurements:

$$\text{carbon paste}\left|\begin{array}{l}\mathrm{NaCF_3CO_2}\ (0.10 - X\ \mathrm{M})\\ \mathrm{CF_3CO_2H}\ (X\ \mathrm{M})\\ \mathrm{Ru(II)}\ (10^{-3}\ \mathrm{M})\end{array}\right\|\begin{array}{c}\mathrm{NaCl}\\ \mathrm{(satd)}\end{array}\left\|\ \mathrm{SCE}\right.$$

Formal potentials E_f were measured as the mean of the anodic and cathodic peaks. Potentials were measured against a SCE and were converted to the NHE reference by adding 242 mV. The reversibility of the systems was judged by applying two criteria: (i) comparing the ratio of the peak current for the cathodic process relative to the peak current for the anodic process;[23] (ii) comparing the peak-to-peak separation with that of a system known to be reversible; i.e., $Ru(NH_3)_6^{3+}$–$Ru(NH_3)_6^{2+}$.[24]

(d) Kinetic Experiments. Though the phosphite complexes are not very air sensitive, all the solutions employed were degassed with argon, and care was taken in the manipulations to avoid exposure of the samples to oxygen.

Reactions which were slow enough were followed using the Cary 15, Cary 14, or Beckman Acta MVII recording spectrophotometer. The reactions were studied under pseudo-first-order conditions (ligand in large excess) and the pseudo-first-order rate constants k_{obsd} were determined graphically by plotting log $(A_\infty - A_t)$ vs. time (where A_∞ and A_t are the final absorbance value and that at time t, respectively).

The rate of loss of the ligand was measured in some cases by using a high concentration of a competitor ligand to eliminate the reverse reaction (imN for the diphosphite complex and isn for the imN complex). The reactions were performed by dissolving the solids *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2](CF_3SO_3)_2$ or *trans*-$[Ru(NH_3)_4P(OEt)_3(imN)](PF_6)_2$ in concentrated aqueous solutions of the competitor ligand, with the pH, ionic strengths, and temperature having been previously adjusted. The rate of ligand loss was also obtained in an alkaline solution as reaction medium, using a competitor ligand.

For the determination of the rate of loss of SO_3^{2-} from *trans*-$[Ru(NH_3)_4(SO_3)P(OEt)_3]$, the complex was generated in solution. An aliquot of this solution was transferred, using syringe techniques, to a spectrophotometric cell containing a concentrated imidazole solution with pH, ionic strength, and temperature having been adjusted. In all these cases, care was taken to keep the concentration of the complex low enough ($(2–5) \times 10^{-6}$ M), so that the contribution of the back-reaction could be disregarded.

For rapid reactions, an Aminco stopped-flow apparatus was used. A Nova 2 computer connected with the stopped-flow system provided for data acquisition and analysis. The reactions were studied under pseudo-first-order conditions and the experimental data analyzed using a program devised by H. Krentzien and G. Brown.[21] At the same time, the absorbance change was followed on an Omnigraphic 200 X-Recorder or on a Tektronix 5102N/D11 oscilloscope. When necessary, a Model C5 Polaroid camera with Polaroid film was used to record the oscilloscope trace. The specific rates thus acquired were in good agreement with those obtained from the computer.

(e) Treatment of Data. First-order or pseudo-first-order rate constants were obtained in virtually all the experiments, whether association of ligand with *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ or loss of ligand from the resulting complex was being studied. These are in every case designated as k_{obsd}. For $P(OEt)_3$, SO_3^{2-}, and imN as entering ligands, conversion of Ru(II) to the complex is virtually complete at equilibrium, and plots of k_{obsd} vs. [L] show a zero intercept. The association quotients were then evaluated by taking the ratio of k_{obsd} forward to k_{obsd} reverse, the latter determined using a competitor ligand. For isn, pyr, and $Mepyr^+$ as entering ligands, the plots of k_{obsd} vs. [L] show a positive intercept at [L] = 0, implying that in these cases conversion to the ligand complexes is incomplete at equilibrium. Approach to equilibrium is then governed by

$$k_{obsd} = k_1[L] + k_{-1}$$

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

The specific rate k_1 was evaluated from the limiting slope at low [L] (the curvatures shown in the plots will be dealt with in the Discussion) and k_{-1} from the intercept.

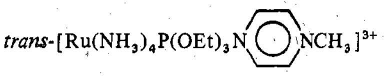
Results

(1) Absorption Spectra. In Table I the results of the spectrophotometric measurements of the new species prepared in the course of this work are summarized. Figure 1 shows the absorption characteristics for *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$.

(2) The Formation of *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$. The title ion is not formed in significant amounts with either $[Ru(NH_3)_5(H_2O)]^{2+}$ or *trans*-$[Ru(NH_3)_4(SO_2)(H_2O)]^{2+}$ as starting material. When equimolar amounts of the latter ion and triethyl phosphite react, the bis(phosphito) species is formed, with some of the SO_2 complex remaining at the end of the reaction. Acetone rather than water was used as solvent to increase the solubility of the ligand and to reduce the rate of ligand hydrolysis, which is quite rapid for the free ligand in acidic aqueous solution.[5,25,26]

When left in acidic solution, *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ changes essentially quantitatively to *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$. In following the change spectrophoto-

Table I. UV-Vis Band Maxima and Molar Absorptivities for the Phosphite Complexes

Complex	λ, nm[a]	ε, M^{-1} cm^{-1}	Conditions
trans-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$	262 294	(4.4 ± 0.2) × 10^2 (2.4 ± 0.2) × 10^2	0.10 M NaCl or $NaCF_3CO_2$, $[H^+] = 10^{-1}$–$10^{-5.5}$ M
trans-$[Ru(NH_3)_4(H_2O)P(OEt)_3]^{2+}$	316	(6.50 ± 0.15) × 10^2	0.10 M NaCl or $NaCF_3CO_2$, $[H^+] = 10^{-1}$–$10^{-5.5}$ M
trans-$[Ru(NH_3)_4P(OEt)_3(isn)]^{2+}$	350	(4.8 ± 1) × 10^3	0.10 M NaCl or $NaCF_3CO_2$, $[H^+] = 10^{-3}$ M, 0.80 M isn
trans-$[Ru(NH_3)_4P(OEt)_3(pyr)]^{2+}$	366	(4.2 ± 1) × 10^3	0.10 M NaCl or $NaCF_3CO_2$, $[H^+] = 10^{-3}$ M, 2.0 M pyr
trans-$[Ru(NH_3)_4P(OEt)_3(imN)]^{2+}$	303	(5.2 ± 0.1) × 10^2	0.10 M $NaCF_3CO_2$, 0.20 M imN
 *trans*-$[Ru(NH_3)_4P(OEt)_3NC_5H_4NCH_3]^{3+}$	525		0.70 M $NaCF_3CO_2$, 0.2 M $Mepyr^+$,[b] $[H^+] = 10^{-5.6}$ M
trans-$[Ru(NH_3)_4P(OEt)_3(SO_3)]$	300	(3.5 ± 0.1) × 10^2	0.20 M Na_2SO_3, 0.30 M $NaCF_3CO_2$, $[H^+] = 10^{-9.2}$ M[c]

[a] With an uncertainty of ±1 nm. [b] Acetate buffer 0.10 M. [c] Borate buffer 0.10 M.

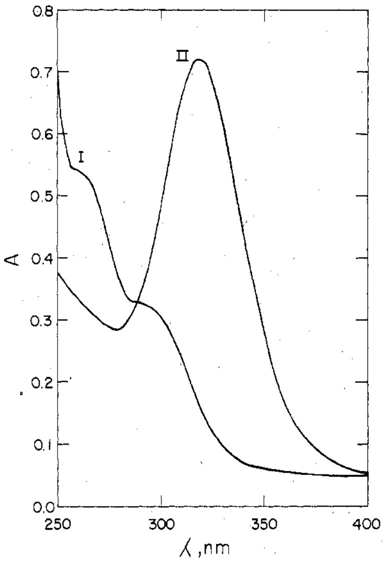


Figure 1. Ultraviolet spectra of (I) *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ and (II) *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$. $\mu = 0.10$ ($NaCF_3CO_2$); $[H]^+ = 10^{-3}$ M^{-1}.

Table II. Aquation Rates for *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ [a]

No.	*T*, °C	$[H^+]$, M	10^5k_{obsd}, s^{-1} [b]
1	25.0 ± 0.1	1.0 × 10^{-1}	2.24
2	25.0 ± 0.1	1.0 × 10^{-2}	2.28
3	25.0 ± 0.1	1.0 × 10^{-3}	2.26
4	25.0 ± 0.1	2.0 × 10^{-5}	2.23
5	25.0 ± 0.1	1.0 × 10^{-3}	2.0[c]
6	35.0 ± 0.1	1.0 × 10^{-3}	9.4
7	35.0 ± 0.1	9.0 × 10^{-10}	0.604
8	35.0 ± 0.1	9.0 × 10^{-10}	7.7[d]
9	35.0 ± 0.1	9.0 × 10^{-10}	8.8[e]
10	45.0 ± 0.1	1.0 × 10^{-3}	47.8

[a] $\mu = 0.10$ ($NaCF_3CO_2$); [Ru(II)] = 1.0 × 10^{-3} M. $\Delta H^{\ddagger} = 28.1 \pm 0.3$ kcal/mol; $\Delta S^{\ddagger} = 15 \pm 1$ cal deg^{-1} mol^{-1}. [b] Each value is a mean of at least three independent determinations agreeing better than 97%. [c] Measured by cyclic voltammetry. [d] [imN] = 0.7 M. [e] [imN] = 1.6 M.

Table III. The Reaction of $P(OEt)_3$ with *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ [a]

$10^3[P(OEt)_3]$, M	10^3k_{obsd}, s^{-1}	k_1, M^{-1} s^{-1}
5.37	4.1	0.77
2.69	1.98	0.74
3.21	2.36	0.73
4.02	3.00	0.75

[a] [Ru(II)] = 2.2 × 10^{-4} M; water–ethanol, 85:15 by volume; 0.05 M $NaCF_3CO_2$, 0.05 M $NaHCO_3$.

metrically, an isosbestic point was observed at λ 289 nm, which persisted for more than 4 half-lives.

The kinetic experiments on the formation of the monophosphite complex are summarized in Table II. The reaction is first order in the concentration of the diphosphite complex. The rate is independent of acid concentration over a wide range but does become significantly slower in alkaline solution (cf. no. 6 and 7, Table II). In acidic solution, the phosphite ligand hydrolyzes to $HPO(OEt)_2$ as rapidly as it is formed, but it persists in alkaline solution for longer periods of time.[27] When imidazole is added as a competing ligand, the rate of phosphite loss in alkaline solution approaches the value measured in acidic solution.

A solution containing *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ was titrated with standard NaOH. There was no evidence for consumption by the ion of OH^- below a pH of 11.5. Furthermore, there is no significant change in the absorption spectrum of a solution below pH 11.5 and we can conclude that pK_a for the coordinated water lies higher than 11.5.

(3) Substitution in $[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$. (a) Triethyl Phosphite as Ligand. The rate of reaction 1 was measured

$$trans\text{-}[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} + P(OEt)_3 = trans\text{-}[Ru(NH_3)_4(P(OEt)_3)_2]^{2+} + H_2O \quad (1)$$

in water–ethanol (85:15 by volume). The ionic strength was kept at 0.10 (0.050 M $NaCF_3CO_2$, 0.050 M $NaHCO_3$). For each experiment, a fresh stock solution of $P(OEt)_3$ was prepared and was then used with dispatch. When the ligand solution was kept even for 40 min at room temperature, the specific rates were 7% lower than those measured for a freshly prepared solution, presumably because there had been significant hydrolysis during storage. In evaluating the kinetic results, it should be kept in mind that Allen and Ford[28] have noted that for a number of reactions involving substitution on $[Ru(NH_3)_5(H_2O)]^{2+}$ rates in water–ethanol (88:12) were not significantly different from those obtained in water. The experimental results are summarized in Table III. Owing to the limited solubility of the ligand, its concentration could not be varied over a wide range.

The specific rate of entry by $P(OEt)_3$ at 25 °C and for the conditions stipulated is 7.5 × 10^{-1} M^{-1} s^{-1}. Because the rate of phosphite loss under conditions where the ligand tends to persist, as measured in basic solution in the presence of imidazole, is the same as that obtained in acidic solution, it can be taken as proven that in the transformation of the bis(phosphite) to the mono(phosphite) complex the rate of the reverse of reaction 1 was being measured, rather than ligand hydrolysis followed by loss of diethyl phosphite. After the rates

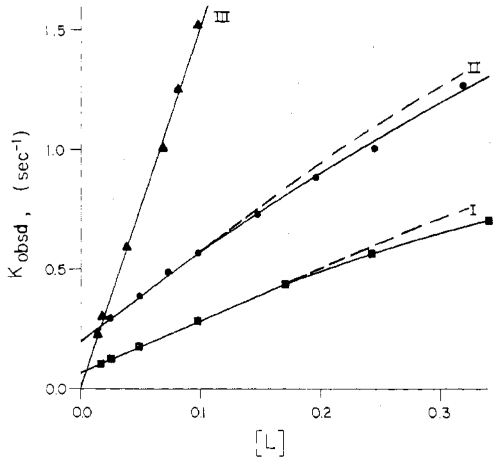


Figure 2. Dependence of k_{obsd} on ligand concentration for the reaction of *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ with: (I) isn, ■; (II) pyr, ●; (III) imN, ▲. $\mu = 0.10$ ($NaCF_3CO_2$), 25 °C.

of the forward and reverse reactions are combined, the equilibrium quotient for reaction 1 at 25 °C is calculated as 3.3×10^4.

The cyclic voltammograms for both the bis- and mono(phosphite) species are reversible. The values of E_f determined from them are 0.88 ± 0.01 and 0.70 ± 0.01 V vs. NHE for the respective couples (25 ± 0.02 °C $\mu = 0.10$, $[H^+] = 10^{-1}$–10^{-4} M).

On combining the values of E_f for the bis(phosphite) couple with the equilibrium constant for reaction 1, that for reaction 2 is calculated as 30. By using the values of E_f for $[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$–$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ and for $[Ru(NH_3)_4(H_2O)_2]^{3+}$–$[Ru(NH_3)_4(H_2O)]^{2+}$,[29] the affinity of Ru(II) in *trans*-$[Ru(NH_3)_4(H_2O)_2]^{2+}$ for phosphite is calculated as being 3×10^{11}-fold greater than that of Ru(III) in the same environment. It is altogether likely that when water is replaced in *trans*-$[Ru(NH_3)_4(H_2O)_2]^{3+}$ the equilibrium quotient for the first phosphite is greater than that for the second and thus a lower limit of 10^{13} is calculated for the equilibrium quotient for reaction 3.

$$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} + P(OEt)_3 = [Ru(NH_3)_4(P(OEt)_3)_2]^{2+} + H_2O \quad (2)$$

$$trans\text{-}[Ru(NH_3)_4(H_2O)_2]^{2+} + P(OEt)_3 = trans\text{-}[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} + H_2O \quad (3)$$

(b) Isonicotinamide (isn) as Ligand. The data obtained for isn in reaction with *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ are summarized in Table IV, and in Figure 2, the values of the pseudo-first-order specific rates (ligand in excess) are shown plotted against the concentration of the entering ligand. Most of the experiments were done at a pH high enough so that the ligand was largely in the base form ($pK_a(isnH^+) = 3.5$).[30] Experiments done at lower pH suggest that $isnH^+$ also is reactive as a substituent[31] but less so than isn; insufficient data were obtained to extract a dependable value for the specific rate of substitution for the cation.

From the plot of k_{obsd} vs. [L], k_1 and k_{-1} at 25.0 °C are evaluated as 2.26 M^{-1} s^{-1} and 6.4×10^{-2} s^{-1}, respectively, leading to a value of 35 for the equilibrium quotient governing the association at the given temperature. The affinity of isn for Ru(II) in the phosphite complex is low enough to make feasible the direct determination of ligand loss. The measurement was made by dissolving the solid in dilute solution (acetate buffer, pH 5.2, $\mu = 0.1$) and following the absorption at 25 °C. The values of k_{-1} thus measured in two experiments were 6.1×10^{-2} and 6.3×10^{-2} s^{-1}. Furthermore, the equilibrium quotient was determined directly by spectrophotometry on an equilibrium mixture and the value thus obtained was 37.

Table IV. Substitution in *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ by Isonicotinamide[a]

T, °C	10^2[isn],[b] M	pH	$10k_{obsd}$,[c] s^{-1}
25.0 ± 0.2	1.69	5.1	1.01
25.0 ± 0.2	2.45	5.1	1.24
25.0 ± 0.2	4.85	5.1	1.72
25.0 ± 0.2	9.70	5.1	2.83
25.0 ± 0.2	17.0	5.1	4.35
25.0 ± 0.2	2.42	5.1	5.65
25.0 ± 0.2	3.40	5.1	7.01
25.0 ± 0.2	4.43	5.1	8.60
25.0 ± 0.2	24.5	5.6	1.25
25.0 ± 0.2	24.5	4.4	1.13
34.7 ± 0.2	2.00	5.6	3.44
34.7 ± 0.2	4.00	5.6	4.56
34.7 ± 0.2	6.00	5.6	5.55
34.7 ± 0.2	8.00	5.6	6.67
16.0 ± 0.2	3.50	5.6	0.456
16.0 ± 0.2	5.00	5.6	0.562
16.0 ± 0.2	6.50	5.6	0.705
16.0 ± 0.2	8.00	5.6	0.805

[a] $\mu = 0.10$ ($NaCF_3CO_2$); [Ru(II)] = 1.5×10^{-4} M. [b] Concentration of unprotonated form, calculated from stoichiometric concentration using pK_a for isn as 3.5. [c] Each value is a mean of at least three independent determinations agreeing within 3%.

Table V. Substitution in *trans*-$[Ru(NH_3)_4(P(OEt)_3(H_2O)]^{2+}$ by Pyrazine[a]

T, °C	10^2[pyr], M	$10k_{obsd}$,[b] s^{-1}
25.0 ± 0.2	2.45	2.97
25.0 ± 0.2	4.90	3.78
25.0 ± 0.2	7.35	4.83
25.0 ± 0.2	9.80	5.65
25.0 ± 0.2	14.7	7.27
25.0 ± 0.2	19.6	8.85
25.0 ± 0.2	24.5	10.1
25.0 ± 0.2	31.8	12.7
25.0 ± 0.2	39.2	14.0
25.0 ± 0.2	54.9	18.2
35.0 ± 0.2	3.38	10.0
35.0 ± 0.2	4.04	10.7
35.0 ± 0.2	6.07	12.8
35.0 ± 0.2	8.01	14.1
16.1 ± 0.2	3.00	0.964
16.1 ± 0.2	4.72	1.18
16.1 ± 0.2	6.00	1.29
16.1 ± 0.2	7.50	1.45

[a] $\mu = 0.10$ ($NaCF_3CO_2$); pH 5.6; [Ru(II)] = 1.5×10^{-4} M. [b] Each value is a mean of at least three independent determinations agreeing within 3%.

The values of k_1 and k_{-1} at 16.0 ± 0.2 °C are 0.79 ± 0.01 M^{-1} s^{-1} and (1.76 ± 0.01) × 10^{-2} s^{-1}, and at 34.7 ± 0.2 °C they are 5.33 ± 0.07 M^{-1} s^{-1} and (2.37 ± 0.03) × 10^{-1} s^{-1}. From the data at three temperatures, the enthalpies and entropies of activation are calculated as $\Delta H^{\ddagger} = 17.5 \pm 0.7$ kcal, $\Delta S^{\ddagger} = 1.7 \pm 1$ cal deg^{-1} mol^{-1}, $\Delta H^{\ddagger}_{-1} = 23.5 \pm 0.7$ kcal, and $\Delta S^{\ddagger}_{-1} = 14.6 \pm 1$ cal deg^{-1} mol^{-1}. The net replacement of H_2O trans to $P(OEt)_3$ by isn is exothermic by 6.0 ± 1.4 kcal mol^{-1}, and the entropy change accompanying the reaction is 12.9 ± 2 cal mol^{-1} deg^{-1} (these data are calculated from the equilibrium quotients as a function of temperature).

The equilibrium solutions for *trans*-$[Ru(NH_3)_4P(OEt)_3(isn)]^{2+}$ are quite stable (the absorbance of the product solution changes less than 2% in 1 h) indicating that ligand reduction is not a serious complication.

(c) Pyrazine (pyr) as Ligand. In Table V are summarized the data obtained with pyrazine as the entering ligand. The pH was high enough throughout the series so that the ligand was virtually completely unprotonated. The values of k_{obsd}

Table VI. Substitution in *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ by Methylpyrazinium Ion[a]

$[Mepyr^+]$, M	k_{obsd},[b] s^{-1}	$[Mepyr^+]$, M	k_{obsd},[b] s^{-1}
0.0250	7.14	0.100	8.70
0.0350	7.86	0.200	8.91
0.0500	7.76	0.300	9.05
0.0750	8.18		

[a] $\mu = 1.0$ $(NaCF_3CO_2)$; $T = 25.2 \pm 0.2$ °C; pH 4.7; $[Ru(II)] = 1.5 \times 10^{-4}$ M. [b] Each value is a mean of at least three independent determinations agreeing within 4%.

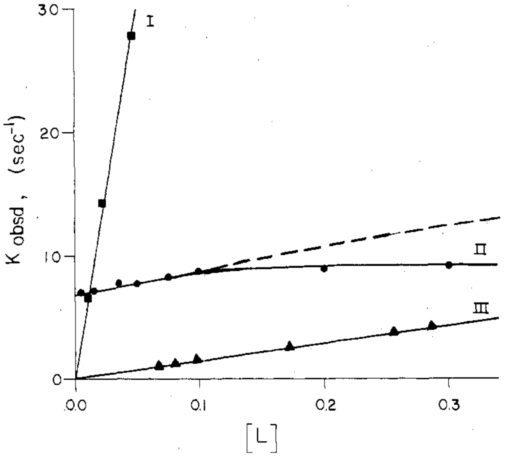


Figure 3. Dependence of k_{obsd} on ligand concentration for the reaction of *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ with: (I) SO_3^{2-}, ■; (II) $Mepyr^+$, ●; (III) imN, ▲. Conditions: I and II, $\mu = 1.0$ $(NaCF_3CO_2)$, 25 °C; III, $\mu = 0.10$ $(NaCF_3CO_2)$, 25 °C.

plotted as a function of [pyr] are shown in Figure 2.

Taking account of the intercept and the slope when [L] is small, the data in Figure 2 lead to values of 3.8 M^{-1} s^{-1} and 0.205 ± 0.002 s^{-1} for k_1 and k_{-1} and an equilibrium quotient of 19, all at 25.2 ± 0.2 °C. Direct measurement of the equilibrium quotient by the method used for isn gave a value of 15 at 25 °C. At 16.1 ± 0.2 °C, $k_1 = 1.20 \pm 0.02$ M^{-1} s^{-1} and $k_{-1} = (6.50 \pm 0.07) \times 10^{-2}$ s^{-1}; at 35.0 ± 0.1 °C, $k_1 = 10.4 \pm 0.9$ M^{-1} s^{-1} and $k_{-1} = 0.64 \pm 0.03$ s^{-1}. The enthalpy changes $\Delta H_1^{\ddagger}$, $\Delta H_{-1}^{\ddagger}$, and ΔH_{eq} are calculated as 19.5 ± 0.7, 20.8 ± 0.7, and -1.3 ± 1.4 kcal and the corresponding entropy changes as 9.4 ± 1, 9.0 ± 1, and 0.4 ± 2 cal deg^{-1} mol^{-1}.

(d) Methylpyrazinium Ion ($Mepyr^+$) as Ligand. The data on the $Mepyr^+$ system are summarized in Table VI and are shown graphically in Figure 3. The plot of k_{obsd} vs. $[Mepyr^+]$ in this case shows striking deviations from linearity. Since $Mepyr^+$ can function as an oxidizing agent, it seemed important to determine whether Ru(III) was formed. On adding $Ru(NH_3)_6^{2+}$ to the product solution—this reducing agent is strong enough to convert any Ru(III) products which might reasonably be expected to form to Ru(II)—no increase in the absorption due to Ru(II)–$Mepyr^+$ species was observed, and we conclude that no significant oxidation by $Mepyr^+$ occurs.

By using slopes and intercepts as before, the values of k_1, k_{-1}, and K_{eq} obtained for $Mepyr^+$ are 57 M^{-1} s^{-1}, 6.1 s^{-1}, and 9.3, at 25 °C.

(e) Imidazole (imN) as Ligand. The data for imN as entering ligand are summarized in Table VII and are plotted in Figure 3. In contrast to the plots for the π-acid ligands isn, pyr, and $Mepyr^+$, the plot of k_{obsd} vs. [imN] is linear over the whole concentration range.

Table VII. Substitution in *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]$ by Imidazole[a]

T, °C	10^2[imN],[b] M	pH	k_{obsd},[c] s^{-1}	k_1, M^{-1} s^{-1}
25.0 ± 0.2	1.43	8.6	0.226	15.8
25.0 ± 0.2	1.91	8.6	0.306	16.0
25.0 ± 0.2	3.82	8.6	0.590	15.6
25.0 ± 0.2	6.68	8.6	1.01	15.3
25.0 ± 0.2	8.02	8.6	1.25	15.6
25.0 ± 0.2	9.74	8.6	1.52	15.6
25.0 ± 0.2	17.2	8.6	2.56	14.9
25.0 ± 0.2	25.6	8.6	3.77	14.7
25.0 ± 0.2	28.6	8.6	4.21	14.7
25.0 ± 0.2	38.2	8.6	5.43	14.2
25.0 ± 0.2	47.7	8.6	6.72	14.2
25.0 ± 0.2	1.25	7.1	0.190	15.1
25.0 ± 0.2	2.50	7.1	0.388	15.6
25.0 ± 0.2	3.75	7.1	0.607	16.2
25.0 ± 0.2	5.00	7.1	0.765	15.3
13.8 ± 0.2	1.91	8.6	0.100	5.2
13.8 ± 0.2	3.82	8.6	0.198	5.2
13.8 ± 0.2	5.73	8.6	0.301	5.2
13.8 ± 0.2	7.64	8.6	0.390	5.1
34.8 ± 0.2	1.91	8.6	0.676	35.4
34.8 ± 0.2	3.82	8.6	1.37	38.9
34.8 ± 0.2	5.73	8.6	2.12	36.3
34.8 ± 0.2	7.64	8.6	2.81	36.8

[a] $\mu = 0.10$ $(NaCF_3CO_2)$; $[Ru(II)] = 1.1 \times 10^{-3}$ M. [b] Concentrations of free base. [c] Each value is a mean of at least three independent determinations whose agreement is better than 97%.

Table VIII. Aquation Rates for *trans*-$[Ru(NH_3)_4(P(OEt)_3)(imN)]^{2+}$ [a]

T, °C	pH	[isn], M	$10^3 k_{obsd}$,[b] s^{-1}
31.2 ± 0.1	8.6[c]	0.300	23.1
25.0 ± 0.1	8.6[c]	0.200	10.2
25.0 ± 0.1	8.6[c]	0.250	9.64
25.0 ± 0.1	8.6[c]	0.500	9.90
25.0 ± 0.1	8.6[c]	0.600	9.90
25.0 ± 0.1	4.8[d]	0.250	10.0
25.0 ± 0.1	4.8[d]	0.500	10.3
23.3 ± 0.1	8.6[c]	0.300	7.70
14.5 ± 0.1	8.6[c]	0.300	2.53

[a] $[Ru(II)] = 5 \times 10^{-5}$ M. [b] Each value is a mean of at least three independent determinations which agree to better than 3%. [c] $\mu = 0.10$, $NaHCO_3$. [d] $\mu = 0.10$, acetate buffer.

Table IX. Substitution in *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ by Sulfite[a]

$10^2 \cdot [SO_3^{2-}]$, M	k_{obsd},[b] s^{-1}	$10^{-2}k$, M^{-1} s^{-1}	$10^2 \cdot [SO_3^{2-}]$, M	k_{obsd},[b] s^{-1}	$10^{-2}k$, M^{-1} s^{-1}
1.12	6.5	5.8	6.97	42.3	6.1
2.32	14.2	6.1	9.30	53.8	5.7
4.65	27.7	5.9	13.9	80.1	5.8

[a] $\mu = 1.0$ $(NaCF_3CO_2)$; $[Ru(II)] = 1.5 \times 10^{-3}$ M; pH 9.2; 25.2 ± 0.2 °C. [b] Each value is a mean of at least three independent determinations which agree to better than 3%.

The experiments on the rate of loss of imN from *trans*-$[Ru(NH_3)_4P(OEt)_3(imN)]^{2+}$ were done by dissolving a solid containing this ion in a buffered solution of isn. The latter ligand was present at high enough concentration so that it scavenged the aquo ion as it was formed. The reaction rates are again first order in the ruthenium(II) reactant. The data obtained in this phase of the study are summarized in Table VIII.

The values of k_1, k_{-1}, and K_{eq} at 25 °C are 15.2 ± 0.5 M^{-1} s^{-1}, $(9.9 \pm 0.3) \times 10^{-3}$ s^{-1}, and 1.5×10^3.

The specific rate k_1 was determined also at 13.8 ± 0.2 °C (5.14 ± 0.07 M^{-1} s^{-1}) and at 34.8 ± 0.2 °C (37.0 ± 0.5 M^{-1} s^{-1}); k_{-1} was determined at 14.5 ± 0.1 °C ($(2.53 \pm 0.03) \times 10^{-3}$ s^{-1}), 23.3 ± 0.1 °C ($(7.70 \pm 0.09) \times 10^{-3}$ s^{-1}), and 31.2 ± 0.1 °C ($(2.31 \pm 0.04) \times 10^{-2}$ s^{-1}). From these and the room-temperature data, $\Delta H_1^{\ddagger}$ is calculated as 16.1 ± 0.9 kcal, $\Delta H_{-1}^{\ddagger}$ as 20.7 ± 0.9 kcal, $\Delta S_1^{\ddagger}$ as 0.2 ± 0.9 cal mol^{-1} deg^{-1}, and $\Delta S_{-1}^{\ddagger}$ as 1.7 ± 1 cal mol^{-1} deg^{-1}. The replacement of H_2O

Table X. Data on Substitution Reactions of *trans*-$[XRu(NH_3)_4(H_2O)]^{2+}$ with Selected Ligands[a]

X	L	k_1, M^{-1} s^{-1}	k_{-1}, s^{-1}	K_{eq}, M^{-1}	Ref
SO_2	$Mepyr^+$	7×10^{-2}			19
	pyr	3×10^{-2}	8×10^{-4}	40	19
SO_3^{2-}	pyr	13	4.5×10^{-3}	2.9×10^3	19
	imN	43	3.7×10^{-3}	1.2×10^4	14
	isn	23	6.3×10^{-3}	3.8×10^3	19
$P(OEt)_3$[b]	pyr	3.8	2.0×10^{-1}	2.0×10^{-1}	
	imN	15.2	9.9×10^{-3}	1.5×10^3	
	isn	2.24	6.4×10^{-2}	36	
	$Mepyr^+$	57	6.1	9.3	
	SO_3^{2-}	5.9×10^2	7.5×10^{-3}	7.9×10^4	
	$P(OEt)_3$	0.75	1.12×10^{-5}	6.7×10^4	
imC	isn	60	1.2×10^{-1}	6×10^2	36
NH_3	isn	1.05×10^{-1}	$<10^{-9}$	$>1 \times 10^8$	31
	pyr	5.6×10^{-2}			31
	imN	2.0×10^{-1}	7.1×10^{-8}	2.8×10^6	31, 37
	$Mepyr^+$[c]	2.4×10^{-3}			36

[a] At 25 ± 0.2 °C; $\mu = 0.10$. [b] This work. [c] $\mu = 1.0$ $(NaCF_3CO_2)$.

trans to $P(OEt)_3$ by imN is slightly exothermic ($\Delta H_{eq} = -4.6 \pm 1.8$ kcal; $\Delta S_{eq} = -1.5 \pm 1.9$ cal mol^{-1} deg^{-1}).

(f) Sulfite as Ligand. Table IX and Figure 3 show the data obtained with SO_3^{2-} as the entering ligand. The reactions took place at a pH high enough so that at most 0.5% of the sulfite ion was protonated. Akin to the behavior shown by imidazole and different from that of isn, pyr, and $Mepyr^+$, the plot of k_{obsd} against SO_3^{2-} concentration is a straight line.

In measuring the rate of ligand loss, imN was used as the competing ligand at concentrations of 1.0, 1.3, 1.5, and 1.6 M. The values of $k_{obsd} \times 10^3$ (s^{-1}) at 25 °C in these experiments were measured as 7.1, 7.4, 7.5, and 7.5, respectively. After combination of the specific rate for ligand loss, $(7.5 \pm 0.3) \times 10^{-3}$ s^{-1}, with that for ligand entry, $(5.9 \pm 0.2) \times 10^2$ M^{-1} s^{-1}, the equilibrium quotient for the reaction $[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} + SO_3^{2-} = Ru(NH_3)_4P(OEt)_3(SO_3) + H_2O$ is found to be $(8.0 \pm 0.5) \times 10^4$.

4. Attempts to Remove $P(OEt)_3$ by Oxidation. Only a few exploratory experiments were done on this point, but they suffice to show that ligand removal by oxidation is not a facile process. Cyclic voltammetry was used to monitor ligand loss. Treatment of an acidic solution containing *trans*-$[Ru(NH_3)_4P(OEt)_3)_2]^{2+}$ with Br_2, Ce(IV), or H_2O_2 in excess did not produce new species at a rate significantly different from that characteristic of spontaneous ligand loss.

Discussion

No direct observations were made which prove that trans rather than cis species are being dealt with, but this supposition is strongly supported by the fact that when $P(OEt)_3$ is present, a single position in the coordination sphere is labilized and by the general similarity of $P(OEt)_3$ to SO_3^{2-} acting as ligand.

A point of interest in the spectra of the phosphite complexes investigated is the origin of the relatively weak band appearing in the near-UV—294 and 316 nm for the bis(phosphite) and mono(phosphite), respectively. This band is presumably related to that appearing at 343 nm (ϵ 240) in the spectrum of $[Ru(NH_3)_4(SO_3)(H_2O)]$.[19] It is unlikely that these bands are πd–π* transitions. Militating against this assignment is the fact that the bands are weak and the fact that the band for the bis(phosphite) appears at higher energy than that for the mono(phosphite). When isn, pyr, and py are ligands, the assignments as πd–π* are unequivocal, and in every instance the trans bis complex absorbs at lower energy than the monosubstituted one.[32] It should be noted that even $[Ru(NH_3)_5(H_2O)]^{2+}$ shows two bands in the near-UV: 268 nm (ϵ 748 ± 5) and 320 nm (sh) (ϵ 100 ± 3).[29] The latter at least is likely a d–d transition and this is probably the case for the near-UV bands observed for the phosphito and sulfito complexes in the same wavelength range.

When isn, pyr, and $Mepyr^+$ are present as ligands trans to $P(OEt)_3$, bands of much higher intensity are observed in the near-UV–visible region of the spectrum: 350 nm (ϵ 4.8×10^3), 366 nm (ϵ 4.2×10^3), and 520 nm, respectively. For SO_3^{2-} trans to the same three ligands the band characteristics are 417 nm (ϵ 6.6×10^3), 433 nm (ϵ 5.7×10^3), and 580 nm.[19] These bands arise from πd–π* transitions for the N-heterocyclics and the shifts to higher energies compared to those for the pentaammines might be taken to suggest that $P(OEt)_3$ and SO_3^{2-} have a net electron-withdrawing effect compared to NH_3. However, as pointed out earlier,[19] ligands such as these, which labilize selectivity in the trans position, have qualities quite different from those of CO, NO^+, and $Mepyr^+$ which are good π acids but indifferent σ donors. While it may be true that $P(OEt)_3$ has a net electron-withdrawing effect, the shift in band energies may owe something to a structural difference; it seems quite likely that $P(OEt)_3$ and SO_3^{2-} cause an increase in the distance from the metal of the ligand trans to them.

Protonation of pyr on $Ru(NH_3)_5^{2+}$ causes a very small bathochromic shift compared to that produced when pyr on $Fe(CN)_5^{3-}$ is protonated.[33] This apparent "saturation" effect observed for $Ru(NH_3)_5^{2+}$ is undoubtedly related to the fact that this ligand when attached to $Os(NH_3)_5^{2+}$, which is even more electron releasing than $Ru(NH_3)_5^{2+}$, shows a hypsochromic shift on protonation.[34,35] In this context it is interesting to note that a large bathochromic shift on protonating pyr is observed when $P(OEt)_3$ or SO_3^{2-} [19] is situated trans to pyr. If these ligands are considered to be electron withdrawing compared to NH_3, the observations just cited are brought into harmony with other related ones.

In Table X the information on the rates of complex formation and aquation at 25.0 ± 0.2 °C obtained in the phosphite systems is summarized together with data on some related systems. In contrast to ligands such as isn, CO, or N_2, which in $Ru^{II}(NH_3)_4(L)(H_2O)$ exert a delabilizing effect when they replace NH_3,[36] $P(OEt)_3$ is labilizing, at least in the trans position, whether or not the ligand is a normal saturated one such as NH_3 (the strong labilization of trans NH_3 by $P(OEt)_3$ can be inferred from the fact that tetraammines are products, whatever the nature of the entering ligand—i.e., a single position is labilized, even for aquation). In this respect, $P(OEt)_3$ resembles SO_3^{2-} but a difference is to be expected because of, among other factors, the net negative charge on sulfite. Using substitution of H_2O by isn as an indicator of the lability of water trans to a particular group, the labilizing effects for ligands thus far studied are CO, N_2 < isn < py < imN ≈ NH_3 < OH^- < $P(OEt)_3$ < CN^- < SO_3^{2-} < imC. As is documented elsewhere[36] for a large class of ligands which are good π acids but indifferent σ bases, lability decreases as the π-acid strength increases. This behavior can be understood in a rather simple way. Much more difficult to understand are ligands such as SO_3^{2-}, CN^-, and carbon bound imidazole which are strongly trans labilizing. Since conversion of R_2S to SO_3^{2-} changes the S ligand to a labilizing group, the position of $P(OEt)_3$ in the series is not altogether surprising, even though the labilizing effect is not understood.

Both SO_3^{2-} and $P(OEt)_3$ can usefully be regarded as being biphilic, namely, as possessing both substantial σ-base and π-acid strength. The data on the rate of loss of ligands having π-acid character from a position trans to $P(OEt)_3$ as compared to when they are trans to SO_3^{2-} suggest that the former is a somewhat stronger π acid. This is in harmony with the fact that, as already pointed out, the saturated ligand H_2O is less labilized by $P(OEt)_3$ than by SO_3^{2-}. In both cases, it is likely of course that the σ-base and π-acid components to the bonding are not simply additive and that an interaction between the two must be allowed for. Incidentally, the fact that $P(OEt)_3$ has a reasonably high affinity for Ru(III) is support for the supposition that $P(OEt)_3$ is a fairly strong σ base.

No firm conclusions can be based on the comparisons of the values of $\Delta H^{\ddagger}$, as measured in the present series (17.5 ± 0.1, 19.5 ± 0.7, 16.1 ± 0.9 for isn, pyr and imN, respectively), with those for the pentaammine series (17 (estimated), 17.5 ± 0.2, and 16.5 ± 0.5).[31] Better and more extensive data are required before it is profitable to speculate on the significance of the comparisons.

An important issue is raised by the profiles shown in the plots of k_{obsd} vs. [L] in Figures 2 and 3. The tendency to rate saturation at high [L] shown by the curves for isn, pyr, and $Mepyr^+$ cannot be explained by a mechanism of the type

$$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} \rightleftarrows [Ru(NH_3)_4P(OEt)_3]^{2+} + H_2O$$

$$[Ru(NH_3)_4P(OEt)_3]^{3+} + L \rightarrow \text{products}$$

On this basis, the same limiting rate at high ligand concentration should be observed for each of the entering ligands. This is clearly not the case; for SO_3^{2-} as entering ligand, the values of k_{obsd} when SO_3^{2-} is only 0.05 M much exceeds the limiting rate observed for $Mepyr^+$. Furthermore, treatment of the data obtained for isn, pyr, and $Mepyr^+$ ligands according to an S_N1 mechanism shows that the limiting rates for the three systems do not agree (3.8, 6.1, and 9.9 s^{-1}, respectively).

An alternative possibility is that there is significant association of *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ with the three π-acid ligands featured in the study. An effect of this kind has convincing precedent in the reaction of $[Ru(NH_3)_5OH_2]^{2+}$ with $Mepyr^+$ [38] and was manifested, but less strongly, also in studies on substitution into the same complex by other π acids.[31] The reaction sequence

$$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} + L \xrightleftharpoons{K_{os}} [[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}\cdot L]$$

$$[[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}\cdot L] \xrightleftharpoons[k'_{-1}]{k'_1} [Ru(NH_3)_4P(OEt)_3(L)]^{2+} + H_2O$$

under pseudo-first-order conditions (L in excess) is governed by

$$k_{obsd} = \frac{k'_1 K_{os}[L]}{K_{os}[L] + 1} + k'_{-1}$$

or

$$\frac{1}{k_{obsd} - k'_{-1}} = \frac{1}{k'_1} + \frac{1}{k'_1 K_{os}[L]}$$

The values of k'_{-1} are the intercepts in the plots of k_{obsd} vs. [L], and so from the plots of $1/(k_{obsd} - k'_{-1})$ vs. 1/[L], k'_1 and K_{os} can be evaluated. For isn, pyr, and $Mepyr^+$, respectively, k'_1 is 4.5, 6.9, and 4.4 s^{-1} and K_{os} is 0.51, 0.54, and 13. The last value is close to that observed for the outer-sphere association of $[Ru(NH_3)_5(H_2O)]^{2+}$ with $Mepyr^+$. Presumably the stability of the outer-sphere complexes owes much to charge transfer from Ru(II) to the π-acid ligand.

The association of the three ligands with *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ indicated by the kinetic data says nothing about the mechanism of substitution itself—it is hardly surprising that the activated complex contains one of each of the metal complex and of the ligand. While the close correspondence of the values of k'_1 for isn, pyr, and $Mepyr^+$—i.e., the specific rates which apply when the rates are expressed in terms of the outer-sphere complexes to the inner-sphere forms—for the three π-acid ligands suggests that bond making is not important in these three cases, this conclusion does not apply to the other ligands. The rate data for imN and SO_3^{2-} show no evidence of rate saturation, and so 1.0 can be considered as a generous upper limit on the quotients governing the outer-sphere association in each case. On this basis, the lower limits on the values of k'_1—i.e., the specific rates for collapse of the outer-sphere ions to the inner-sphere forms—are 15 and 6.1×10^2 s^{-1} for these ligands, respectively. The conclusion seems unavoidable that there is considerable bond making in the activated complexes at least for substitution by the nucleophilic species imN and SO_3^{2-}. This may well be less prominent for isn, pyr, and $Mepyr^+$ which are more weakly nucleophilic.

If bond making is substantial in the activated complexes for reaction, direct replacement of one ligand for another might be expected. No evidence for such a reaction was obtained in any of the experiments in which ligand L was lost in the presence of L′ (L = $P(OEt)_3$ with L′ = imN; L = SO_3^{2-} with L′ = imN; L = imN with L′ = isn). Apparently, the solvent water still plays a special role, in part because of its abundance but in part probably also because of its relatively small size.

Acknowledgment. D.W.F. expresses his thanks for fellowship support from F.A.P.E., Sao Paulo, Brazil, during his tenure at Stanford. Support of the research by NIH Grant GM13868 is also gratefully acknowledged.

Registry No. $[Ru(NH_3)_5(H_2O)](PF_6)_2$, 34843-18-0; $[Ru(NH_3)_5(H_2O)](CF_3SO_3)_3$, 53195-18-9; *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2](PF_6)_2$, 64939-01-1; *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2](CF_3SO_3)_2$, 64939-02-2; *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_2$, 64939-04-4; *trans*-$[Ru(NH_3)_4P(OEt)_3(isn)](PF_6)_2$, 64939-06-6; *trans*-$[Ru(NH_3)_4P(OEt)_3(imN)](PF_6)_2$, 64939-08-8; *trans*-$[Ru(NH_3)_4P(OEt)_3(pyr)](PF_6)_2$, 64939-10-2; *trans*-$[Ru(NH_3)_4P(OEt)_3(Mepyr)]^{3+}$, 64939-11-3; *trans*-$[Ru(NH_3)_4P(OEt)_3(SO_3)]$, 64939-22-6; isn, 1453-82-3; pyr, 290-37-9; $Mepyr^+$, 17066-96-5; imN, 288-32-4; SO_3^{2-}, 14265-45-3; SO_2, 7446-09-5; $P(OEt)_3$, 122-52-1; H_2O, 7732-18-5; NH_3, 7664-41-7; *trans*-$[Ru(NH_3)_4(SO_2)(H_2O)](CF_3SO_3)_2$, 64939-23-7.

References and Notes

(1) A. Pidcock, "Aspects of Inorganic Chemistry", C. A. McAuliffe, Ed., Halsted Press, New York, N.Y., 1973, pp 1–29.
(2) K. K. Chow, W. Levason, and C. A. McAuliffe, ref 1, pp 35–177.
(3) J. G. Verkade and K. J. Coskran, "Organic Phosphorus Compounds", Vol. 2, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y., 1972, Chapter 3B, pp 1–187.
(4) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).
(5) W. Gerrard and H. R. Hudson, "Organic Phosphorus Compounds", Vol. 5, G. M. Kosolapoff and L. Maier, Ed., Wiley-Interscience, New York, N.Y. 1975, pp 21–302.
(6) R. F. Hudson, "Structure and Mechanism in Organo-phosphorus Chemistry", Academic Press, London, 1965.
(7) R. G. Wilkins, "The Study of Kinetics and Mechanisms of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, Mass., 1974.
(8) In this laboratory the first attempts in this direction were carried out by H. Yamamoto and S. S. Isied, the work indicating that reaction of

$[Ru(NH_3)_5(H_2O)]^{2+}$ with phosphite produces a bis rather than a mono complex.

(9) P. G. Douglas and B. L. Shaw, *J. Chem. Soc. A*, 1556 (1970).

(10) D. A. Couch and S. D. Robinson, *Inorg. Nucl. Chem. Lett.*, **9**, 1079 (1973).

(11) D. A. Couch and S. D. Robinson, *Inorg. Chim. Acta*, **9**, 39 (1974).

(12) H. Taube, *Surv. Prog. Chem.*, **6**, 1 (1973).

(13) S. S. Isied, Ph.D. Thesis, Stanford University, 1973.

(14) G. Brown, J. Sutton, and H. Taube, *J. Am. Chem. Soc.*, in press.

(15) R. Magnuson, Ph.D. Thesis, Stanford University, 1974.

(16) A. H. Ford-Moore and B. J. Perry, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 955.

(17) D. E. C. Corbridge, *Top. Phosphorus Chem.*, **6**, 235–365 (1969).

(18) L. H. Vogt, J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965).

(19) S. S. Isied and H. Taube, *Inorg. Chem.*, **13**, 1545 (1974).

(20) C. G. Kuehn and H. Taube, *J. Am. Chem. Soc.*, **98**, 689 (1976).

(21) H. Krentzien, Ph.D. Thesis, Stanford University, 1976.

(22) G. Tom, Ph.D. Thesis, Stanford University, 1975.

(23) R. S. Nicholson, *Anal. Chem.*, **38**, 1406 (1966).

(24) J. B. Headridge, "Electrochemical Techniques for Inorganic Chemists", Academic Press, London, 1969.

(25) A. E. Arbuzof, *Zh. Russ. Fiz.-Khim. O-va.*, **38**, 291 (1960).

(26) D. N. Bernhart and K. H. Rattenbury, *Anal. Chem.*, **28**, 1765 (1956).

(27) M. G. Imaev, *Zh. Obshch. Khim.*, **31**, 1762 (1961).

(28) R. J. Allen and P. C. Ford, *Inorg. Chem.*, **11**, 697 (1972).

(29) H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, **11**, 1460 (1972).

(30) A. Albert, *Phys. Methods Heterocycl. Chem.*, **1**, 68 (1963).

(31) R. E. Shepherd and H. Taube, *Inorg. Chem.*, **12**, 1392 (1973).

(32) A. M. Zwickel and C. Creutz, *Inorg. Chem.*, **10**, 2396 (1971).

(33) H. E. Toma and J. M. Malin, *Inorg. Chem.*, **12**, 1039 (1973).

(34) J. Sen, research in progress. The hypsochromic shift was first observed with $Os(NH_3)_4Cl^+$ as ligand.[35]

(35) R. H. Magnuson and H. Taube, *J. Am. Chem. Soc.*, **97**, 5129 (1975).

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

(37) R. J. Sundberg, R. F. Bryan, I. F. Taylor, Jr., and H. Taube, *J. Am. Chem. Soc.*, **96**, 381 (1974).

(38) J. M. Malin and H. Toma, *J. Am. Chem. Soc.*, **94**, 4039 (1972).

Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Inorganic Derivatives of Iron Sulfide Thiolate Dimers and Tetramers: Synthesis and Properties of the Halide Series $[Fe_2S_2X_4]^{2-}$ and $[Fe_4S_4X_4]^{2-}$ (X = Cl, Br, I)

GEOFFREY B. WONG, M. A. BOBRIK, and R. H. HOLM*

Received July 27, 1977

Entry to new series of binuclear and tetranuclear iron–sulfide–halide dianions is afforded by a combination of reactions of coordinated thiolate and halide displacement. The previously reported complexes $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$ and $[Fe_4S_4(SR)_4]^{2-}$ (R = *t*-Bu, CH_2Ph, Ph) react smoothly with benzoyl halides in acetonitrile to afford $[Fe_2S_2X_4]^{2-}$ and $[Fe_4S_4X_4]^{2-}$ (X = Cl, Br), isolable in good yield as R'_4N^+ salts, and the corresponding thioesters, which have been isolated from representative reactions. Treatment of the chloride complexes with sodium iodide in acetonitrile yields salts of $[Fe_2S_2I_4]^{2-}$ and $[Fe_4S_4I_4]^{2-}$. Recent x-ray structural results for the binuclear and tetranuclear chloride complexes reveal retention of the Fe_2S_2 and Fe_4S_4 core structures present in the thiolate precursors. These are the first complexes containing these core units in which the terminal ligand atoms are not chalcogens. Significant reactions of the halide complexes include conversion to thiolate species with thiol and base and the binuclear–tetranuclear conversions

$$[Fe_2S_2X_4]^{2-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Fe_4S_4X_4]^{2-}$$

effected chemically or electrochemically. Examination of magnetism, redox potentials, and absorption spectra shows that only the first of these properties is essentially independent of halide vs. thiolate terminal ligation at parity of core structure.

Introduction

The binuclear and tetranuclear iron sulfide thiolate complexes of the general types $[Fe_2S_2(SR)_4]^{2-}$ and $[Fe_4S_4(SR)_4]^{2-}$, respectively, have enjoyed substantial utility as minimal representations, or synthetic analogues, of the active sites of iron–sulfur proteins.[1] Apart from their biological context these complexes and the sites which they represent are new members of the classes $M_nA_nL_m$[2] ($m \geq n = 2, 4$) containing substructural or *core* units M_nA_n. However, they differ significantly in structural and electronic features from other members of the same class. While such differences are implicit in our past[1] and continuing[3,4] pursuit of site analogues, several brief comparisons of these species with certain other complexes of the same class serve to emphasize this point.

The binuclear class $M_2A_2L_4$ contains numerous members[5] with the edge-shared bitetrahedral structure of $[Fe_2S_2(SR)_4]^{2-}$[6] (e.g., $[Fe_2S_2(S_2\text{-}o\text{-xyl})_2]^{2-}$, **1**, Figure 1), but only the latter complexes contain the Fe_2S_2 core. This core is found otherwise only in $Fe_2S_2(CO)_6$, a molecule obviously electronically[7] unrelated to and containing a disulfide bond[8] not found in $[Fe_2S_2(SR)_4]^{2-}$. The cubane-type M_4A_4 core geometry is now an unexceptional inorganic stereochemical unit,[9,10] and specific examples of structurally defined Fe_4S_4 cores include those in $[(\eta^5\text{-}C_5H_5)_4Fe_4S_4]$,[11] $[(\eta^5\text{-}C_5H_5)_4Fe_4S_4]^+$,[12] $[(\eta^5\text{-}C_5H_5)_4Fe_4S_4]^{2+}$,[13] $Fe_4S_4(NO)_4$,[14] and $[Fe_4S_4(tfd)_4]^{2-}$.[15] Details of their core structures depart from those of $[Fe_4S_4(SR)_4]^{2-,3-}$[16,17] (**6**), and no core isoelectronic relationships exist between analogue anions and these species.[13,14,16a] Apart from redox behavior[13,14,18] and cleavage of dithiolene tetramers with triphenylphosphine,[18] the reaction chemistry of $[(\eta^5\text{-}C_5H_5)_4Fe_4S_4]^z$, $[Fe_4S_4(NO)_4]^z$, and $[Fe_4S_4(tfd)_4]^z$ species has been little investigated. In particular, there is no information as to whether these complexes can be converted to tetranuclear analogues or other new species by ligand replacement reactions.

Recent experimentation with $[Fe_2S_2(SR)_4]^{2-}$ and $[Fe_4S_4(SR)_4]^{2-}$ complexes has been directed toward an elucidation of their reactivity properties beyond the one-electron redox reactions discovered earlier.[1] While this work is still in a developmental stage examples of two general types of reactions, which proceed with retention or nonretention of core structure, have emerged. Cases of nonretention include dimer–tetramer conversions $[Fe_2S_2(SR)_4]^{2-,3-} \rightarrow [Fe_4S_4(SR)_4]^{2-}$.[4b] Reactions proceeding with core retention necessarily involve alteration of terminal ligands, which have proven to be labile and readily replaceable under ambient conditions in substitution reactions (1)[6] and (2).[16b] Inasmuch as the rate-limiting step in reaction

$$[Fe_2S_2(SR)_4]^{2-} + 4R'SH \rightarrow [Fe_2S_2(SR')_4]^{2-} + 4RSH \tag{1}$$

$$[Fe_4S_4(SR)_4]^{2-} + 4R'SH \rightarrow [Fe_4S_4(SR')_4]^{2-} + 4RSH \tag{2}$$

2 is proposed to be protonation of coordinated thiolate by R'SH,[19] the observation that reaction of $[Fe_4S_4(SEt)_4]^{2-}$ with benzoyl chloride afforded ethylthiobenzoate[20] engaged our attention as another manifestation of nucleophilic reactivity of a thiolate ligand. The present investigation was undertaken to ascertain the fate of the Fe_4S_4 core which, if not disrupted, was expected to appear in the form of $[Fe_4S_4Cl_4]^{2-}$ by analogy

0020-1669/78/1317-0578$01.00/0