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Isonicotinamide as Entering Ligand on *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$, (R = Me, Pr, ^iPr and Bu)

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Abstract

trans-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ (R = Me, Pr, ^iPr, and Bu) reacts with isonicotinamide at second-order-specific rates k_1 of 1.2, 2.3, 7.4 and 8.1 M^{-1} s^{-1} (25 °C, $\mu = 0.10$ $NaCF_3COO/CH_3COOH$), respectively, for R = Me, Pr, ^iPr and Bu. The products *trans*-$[Ru(NH_3)_4P(OR)_3isn](PF_6)_2$ have been isolated and characterized by micro analysis, cyclic voltammetry, and electronic spectral data. The aquation rates k_{-1} for the isonicotinamide (isn) derivatives are 5.2×10^{-2}, 5.9×10^{-2}, 2.0×10^{-1} and 3.4×10^{-1} s^{-1} for R = Me, Pr, Bu and ^iPr, respectively. The activation parameters for the forward and backward reactions indicate the same mechanism for all of them. The substitution proceeds by a dissociative mechanism with a significant outer-sphere association of *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ complexes with isn. Assuming k_1 as indicative of the lability of the coordinated water molecule on the monophosphite complexes, the following sequence of increasing *trans*-effect may be proposed: $P(OMe)_3 < P(OEt)_3 < P(OPr)_3 < P(O^iPr)_3 < P(OBu)_3$. The affinity of the monophosphite complexes for isn increases according to $P(OMe)_3 \simeq P(O^iPr)_3 < P(OEt)_3 < P(OPr)_3 \simeq P(OBu)_3$.

Introduction

Ruthenium(II) complexes exhibit interesting behavior as reagents or catalysts [1, 2]. The majority of these complexes have phosphorus compounds as ancillary ligands [1–3]. Although the phosphorus ligands do not physically contribute to the products of the catalyzed reactions, they play a very important role in determining the activity and selectivity of the catalysts.

Tertiary phosphorus ligands, biphilic in character, have proved to be very effective in ruthenium chemistry in labilizing the ligands in a position *trans* to them, and in stabilizing low oxidation states of the metal center [4–6].

We are engaged in a systematic study of these compounds to obtain an understanding of the basic chemistry of phosphorus compounds in a well-defined octahedral environment. Besides being of interest for its own sake, the knowledge of this area will be equally important as a guide for the selection and the design of 'non-participating' ligand modifications which might enhance the catalytic properties of coordination compounds.

This paper deals with the *trans*-effect and the *trans*-influence of trialkyl-phosphites in the tetraammine complexes of Ru(II). The rates of replacement of water by isonicotinamide in the aquo complexes [7] *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ (R = Me, Et, Pr, ^iPr, Bu) have been used to estimate the *trans*-effect of the phosphite ligands. Up to now we have concentrated most of our attention on small phosphite molecules in an attempt to minimize steric effects and to analyze the changes in the ligand donor–acceptor properties.

Experimental

Reagents

All solvents employed were freshly distilled before use. Phosphites (Aldrich Chemical Co. Inc.) were purified by treatment with metallic sodium and distilled under reduced pressure. Tripropyl phosphite was synthesized from PCl_3 and propanol as described [8] and characterized by NMR, IR and micro analysis. Isonicotinamide (isn), CF_3SO_3H and CF_3COOH were purchased from Aldrich and used without further purification.

Argon, purchased in cylinders from White Martins S/A, was passed first through a gas scrubbing flask of Cr(II) in 0.05 M $HClO_4$ solution over zinc amalgam, and then through water, before bubbling into the desired solution. All glass lines were made using ball and socket joints held tigthly together with clips.

$Ru(NH_3)_6Cl_3$, $[Ru(NH_3)_5Cl]Cl_2$, *trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$ and *trans*-$[Ru(NH_3)_4SO_2(H_2O)](CF_3SO_3)_2$ were prepared as described earlier [4]. The other compounds were prepared as follows:

I. trans-$[Ru(NH_3)_4(P(OR)_3)_2](CF_3SO_3)_2$ *(R = methyl, n-propyl, isopropyl and n-butyl)*

These compounds were synthesized [9] by reacting *trans*-$[Ru(NH_3)_4SO_2(H_2O)](CF_3SO_3)_2$ with the

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desired phosphite in acetone under an argon atmosphere. Excess phosphite and solvent were eliminated by rotoevaporation. The products were purified by recrystallization from acetone and diethyl ether (peroxide-free). All of the complexes were checked for purity by cyclic voltammetry and spectrophotometric [9] measurements. These compounds were stored in a vacuum desiccator and protected from light.

II. *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)](CF_3SO_3)_2$

These complexes were obtained by aquation [4, 5] for 70 h of the corresponding bisphosphite complexes in aqueous solution in the absence of air and light, at 25 ± 3 °C, $C_{H^+} = 1.0 \times 10^{-3}$ M CF_3SO_3H. The 1.0×10^{-3} M CF_3SO_3H solution was degassed for about 30 or 40 min; then a weighed amount of the desired complex was added to the solution. After complete dissolution of the bisphosphite complex, the temperature was held at 25 °C. Dissolution of the higher bisphosphite complexes (R = Bu and ^{i}Pr) was achieved by raising the temperature up to 35 °C.

The *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)](PF_6)_2$ salts were obtained by rotoevaporation of the solvent and were employed in the syntheses of the corresponding isonicotinamide derivatives.

III. *trans*-$[Ru(NH_3)_4P(OR)_3(isn)](PF_6)_2$

The compound obtained in the preceding section, *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)](PF_6)_2$, was dissolved in the minimum volume of the degassed 1×10^{-3} CF_3SO_3H solution. A saturated solution of isonicotinamide and ammonium hexafluorophosphate (1 M isn, 0.4 M NH_4PF_6) was added to the resulting *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ solution. The mixture was stirred, and the yellow–orange precipitate formed was filtered, washed with anhydrous ether (peroxide-free), dried and stored under vacuum.

Kinetic Studies

Reactions between *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ and isonicotinamide were studied under pseudo-first-order conditions with an Aminco stopped-flow instrument. The ligand concentration exceeded that of Ru(II) by at least a factor of 20. After aquation of the bisphosphite complex (60 h), about 2.5 ml of the selected monophosphite sample was transferred, using a glass syringe and platinum needle, to the chamber in the stopped-flow apparatus. The isonicotinamide solution was stored in another chamber. The solutions were kept at the desired temperature for 15 min. The reaction was followed photometrically at 370 nm.

Cyclic Voltammetry

Cyclic voltammograms were obtained using an electrochemical system consisting of Potentiostat/Galvanostat (model-173), Programmer (model-175) and a Recorder (model-RE0074), all obtained from Princeton Applied Research Corporation (PARC). Formal potentials were measured as the mean of the anodic and cathodic peaks. The reversibility of the systems was judged by comparison with the ratio of the peak current for the cathodic process to the peak current for the anodic process. A platinum wire, a SCE and a glassy carbon were employed as auxiliary, reference and working electrodes, respectively.

Treatment of Data

From the absorbance data as function of time, the pseudo-first-order rate constants (k_{obs}) for reaction (1) were determined graphically from plots of $\ln(A_\infty - A_t)$ *vs.* time. Following the treatment, $k_{obs} = k_1[isn] + k_{-1}$, specific second-order rate constants were obtained from plots of the pseudo-first-order rate constants *vs.* the concentration of the ligand in excess.

Results and Discussion

The derivatives *trans*-$[Ru(NH_3)_4P(OR)_3isn](PF_6)_2$, R = Me, Pr, ^{i}Pr and Bu, were characterized by micro analysis (Table I), cyclic voltammetry and electronic spectra (Table II).

The interpretation of the cyclic voltammograms of the monophosphite complexes in the presence of the isonicotinamide is complicated by adsorption effects (for butyl) and by intramolecular electron-transfer reactions. The latter complication occurs after the electrochemical oxidation Ru(II) → Ru(III), which is pH dependent. However, in 0.3 M isn/0.3 M isn H^+ buffer, the cyclic voltammograms for the systems R = Me, Et, Pr and ^{i}Pr are reversible.

All the derivatives of *trans*-$[Ru(NH_3)_4P(OR)_3isn]^{2+}$ exhibit a metal–ligand charge-transfer band, $d_\pi \rightarrow \pi^*$, centered in the 370 nm region of the electronic spectra. The rates of substitution of water in the monophosphite complexes by isn were followed at 370 nm, taking advantage of these metal–ligand charger-transfer M.L.C.T. bands. Tables III–VI summarize the observed rates for the substitution of isonicotinamide in several monophosphite complexes

TABLE I. Micro Analytical Data for *trans*-$[Ru(NH_3)_4P(OR)_3isn](PF_6)_2$

R	% C		% N		% H	
	Calc.	Found	Calc.	Found	Calc.	Found
Me	15.32	15.38	11.91	12.53	3.85	3.95
Pr	22.73	22.63	10.62	11.28	5.34	5.21
^{i}Pr	22.73	23.01	10.62	10.91	5.34	5.50
Bu	26.01	26.37	10.11	10.42	5.45	4.99

TABLE II. UV–Vis Band Maxima, Molar Absorptivities and Formal Potentials for the Phosphite Complex Ions *trans*-$[Ru(NH_3)_4R_1R_2]^{2+}$

R_1	R_2	C_{H^+} (M)	C_{isn} (M)	pH	λ_{max} (nm)	ϵ (M^{-1} cm^{-1})	$E_{1/2}$[a] (V)
$P(OMe)_3$	isn	0.10	0.30	3.6	370[b]	$(5.0 \pm 0.5) \times 10^3$	0.57
$P(OEt)_3$	isn	0.10	0.30	3.6	370[c]	$(4.8 \pm 0.4) \times 10^3$	0.54
$P(OPr)_3$	isn	0.10	0.30	3.6	370	$(4.7 \pm 0.4) \times 10^3$	0.53
$P(O^iPr)_3$	isn	0.10	0.30	3.6	370[b]	$(5.0 \pm 0.5) \times 10^3$	0.49
$P(OPr)_3$	$P(OPr)_3$	0.010		2.0	294	$(2.3 \pm 0.2) \times 10^2$	0.65
$P(OPr)_3$	H_2O	0.010		2.0	316	$(60 \pm 0.3) \times 10^2$	0.46

[a] *vs.* S.C.E., $\mu = 0.10$ (CF_3COOH), 25 ± 0.2 °C, V = 500 mV/s, uncertainty on $E_{1/2} \pm 0.01$ V. [b] Reference [5]. [c] Reference [4].

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

Temperature (°C)	10^2 [isn]	10 k_{obs}[b] (s^{-1})	10^2 k_{-1} (s^{-1})	k_1 (M^{-1} s^{-1})	K_{eq} (M^{-1})
	4.0	0.247			
	6.0	0.313			
	8.0	0.380			
	10.0	0.447			
15 ± 0.1	12.0	0.512	1.14 ± 0.01	0.33 ± 0.01	29.2 ± 0.5
	1.0	0.63			
	2.0	0.75			
	3.0	0.87			
	4.5	1.04			
	6.0	1.22			
	7.5	1.38			
25 ± 0.1	8.0	1.46			
	9.0	1.58			
	12.0	1.93			
	15.0	2.26			
	18.0	2.56			
	24.0	3.16			
	27.0	3.31			
	30.0	3.46	5.20 ± 0.03	1.16 ± 0.05	22.4 ± 0.5
	1.0	1.90			
	2.0	2.09			
	3.0	2.42			
35 ± 0.1	4.0	2.68			
	5.0	2.94			
	6.0	3.19	16.3 ± 0.2	2.61 ± 0.03	16.0 ± 0.4

[a] $\mu = 0.10$ ($NaCF_3COO/CF_3COOH/NaCH_3COO/CH_3COOH$): $C_{Ru(II)} = 5.0 \times 10^{-4}$ M. [b] Each value is a mean of at least four independent determinations agreeing within ±4%.

with different ligand concentrations and different temperatures. The activation parameters for the forward, reverse and overall reactions are given in Table VII.

The large body of information available on substitution reactions of the Ru(II) complex is consistent with the model of a dissociative activation process [4, 7, 10–14]. The plots k_{obs} *vs.* C_L for the substitution reactions of the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ in systems where the entering ligand is isonicotinamide, pyrazine (pyr) or methylpyrazinium ion ($Mepyr^+$) exhibit a departure from linear behavior at ligand concentrations higher than 0.1 M. It has been established [4] that the substantial outer-sphere association is established between the complex *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ and the π-acid entering ligands (isn, pyr and $Mepyr^+$).

This tendency for 'rate saturation' is also observed for the reactions of *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ (where R = Me, Pr, ^{i}Pr and Bu) with isn, and it

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

Temperature (°C)	10^2 [isn]	$10\,k_{obs}$[b] (s^{-1})	$10^2\,k_{-1}$ (s^{-1})	k_1 ($M^{-1}\,s^{-1}$)	K_{eq} (M^{-1})
15 ± 0.1	2.0	0.377	1.87 ± 0.03	0.93 ± 0.02	49 ± 1
	4.0	0.567			
	6.0	0.747			
	8.0	0.933			
25 ± 0.1	1.0	0.823	5.9 ± 0.3	2.33 ± 0.04	39 ± 2
	2.0	1.055			
	3.0	1.296			
	4.0	1.520			
	5.0	1.748			
	8.0	2.449			
35 ± 0.1	3.0	4.323	23 ± 1	6.4 ± 0.3	27 ± 1
	4.0	5.025			
	5.0	5.610			
	6.0	6.303			

[a] μ = 0.10 ($NaCF_3COO/CF_3COOH/NaCH_3COO/CH_3COOH$); $C_{Ru(II)} = 5.0 \times 10^{-4}$ M. [b] Each value is a mean of at least four independent determinations agreeing within ± 3%.

TABLE V. Substitution in *trans*-[$Ru(NH_3)_4P(O^iPr)_3(H_2O)$]$^{2+}$ by Isonicotinamide[a]

Temperature (°C)	10^2 [isn]	$10\,k_{obs}$[b] (s^{-1})	$10^2\,k_{-1}$ (s^{-1})	k_1 ($M^{-1}\,s^{-1}$)	K_{eq} (M^{-1})
15 ± 0.1	1.0	0.137	10.6 ± 0.2	3.1 ± 0.1	29 ± 1
	2.0	0.173			
	3.0	0.200			
	4.0	0.230			
	5.0	0.264			
	6.0	0.295			
25 ± 0.1	2.0	0.490	34 ± 3	7.4 ± 0.1	21 ± 1.2
	3.0	0.561			
	4.0	0.631			
	5.0	0.726			
	6.0	0.781			
	8.0	0.886			
	10.0	0.952			
35 ± 0.1	2.0	1.28	100 ± 5	12.6 ± 0.4	12.6 ± 0.7
	3.0	1.37			
	4.0	1.51			
	5.0	1.62			
	6.0	1.72			
45 ± 0.1	2.0	2.89	238 ± 10	23.1 ± 0.8	9.7 ± 0.3
	3.0	3.08			
	4.0	3.34			
	5.0	3.57			
	6.0	3.79			

[a] μ = 0.10 ($NaCF_3COO/CF_3COOH/NaCH_3COO/CH_3COOH$); $C_{Ru(II)} = 5.0 \times 10^{-4}$ M. [b] Each value is a mean of at least four independent determinations agreeing within ± 8%.

strongly suggests that a dissociative mechanism is operative in such reactions [12, 13].

A good linear relation is observed in the plots of $\Delta H_1^{\neq}$ *vs.* $\Delta S_1^{\neq}$ and $\Delta H_{-1}^{\neq}$ *vs.* $\Delta S_{-1}^{\neq}$ for R = Me, Et, Pr, ^{i}Pr and Bu. These isokinetic plots, ($\Delta G_1^{\neq} = 16.7$ kcal/mol), ($\Delta G_{-1}^{\neq} = 18.9$ kcal/mol), are good evidence [12, 14] that all these reactions follow the same mechanism.

Since a dissociative activation process is taking place, it is reasonable to assume that the second-order

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

Temperature (°C)	10^2 [isn]	$10\ k_{obs}$[b] (s^{-1})	$10^2\ k_{-1}$ (s^{-1})	k_1 ($M^{-1}\ s^{-1}$)	K_{eq} (M^{-1})
15 ± 0.1	2.0	1.61	7.1 ± 0.2	4.43 ± 0.09	63 ± 2
	3.0	2.06			
	4.0	2.49			
	5.0	2.94			
25 ± 0.1	1.0	2.81	19.9 ± 0.4	8.1 ± 0.5	40 ± 3
	2.0	3.64			
	3.0	4.41			
	4.0	5.23			
	5.0	5.55			
	6.0	5.90			
	8.0	6.30			
35 ± 0.1	1.0	5.96	45 ± 2	14.3 ± 0.5	31 ± 2
	2.0	7.78			
	3.0	9.56			
	4.0	10.44			
	5.0	11.74			

[a] $\mu = 0.10$ ($NaCF_3COO/CF_3COOH/NaCH_3COOH/CH_3COOH$); $C_{Ru(II)} = 5.0 \times 10^{-4}$ M. [b] Each value is a mean of at least four independent determinations agreeing within ±3%.

TABLE VII. Activation and Thermodynamics Parameters for the Reactions: *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ + isn $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ *trans*-$[Ru(NH_3)_4P(OR)_3(isn)]^{2+} + H_2O$

R	$\Delta H_1^{\neq}$ (kcal/mol)	$\Delta S_1^{\neq}$ (cal deg^{-1} mol^{-1})	$\Delta H_{-1}^{\neq}$ (kcal/mol)	$\Delta S_{-1}^{\neq}$ (cal deg^{-1} mol^{-1})	ΔH_{eq} (kcal/mol)	ΔS_{eq} (cal deg^{-1} mol^{-1})
Methyl	17.9 ± 0.3	2.0 ± 0.9	23 ± 1	12 ± 2	−5 ± 1	−10 ± 2
Ethyl[a]	17.5 ± 0.7	2 ± 1	23.5 ± 0.7	14 ± 1	−6 ± 1	−12 ± 2
Propyl	18.4 ± 0.4	−1.8 ± 1.3	21.5 ± 0.5	8 ± 1	−5.6 ± 0.9	−10 ± 2
Isopropyl	11.4 ± 0.5	−16.4 ± 0.2	18.4 ± 0.2	1.0 ± 0.7	−6.0 ± 0.7	−17 ± 2
Butyl	9.8 ± 0.4	−21 ± 1	15.9 ± 0.5	−8 ± 1	−6.1 ± 0.9	−13 ± 2

[a] Ref. 4.

specific rates reported for the substitution of isn on *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ do provide an ordering for the dissociation of the water molecule on such complexes. On this basis, the *trans*-effect of the phosphites or the order of increment of the lability of the cooordinated water molecule for the series *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ is as follows for R = Me, Et, Pr, ^{i}Pr, Bu: M < Et < Pr < ^{i}Pr < Bu. This *trans*-effect series follows the same order of decreasing of the activation energy, $\Delta H_1^{\neq}$, as for the formation of the activated complex.

Assuming that the weakening of the Ru(II)-isn bond, estimated from the stability constants K_{eq}, is related to the *trans*-influence, the following order could be observed: Me ~ ^{i}Pr > Et > Pr > Bu. For all the phosphites except ^{i}Pr, the rates of aquation correlate inversely with the thermodynamic bond strength of the Ru(II)-isn bond, $\Delta H_{-1}^{\neq}$. Since the *trans*-effect is related to the nature of the transition state, while the *trans*-influence is a ground state phenomenon, it is not surprising that the series above does not follow the same order.

The increase of the σ basicity of the $P(OR)_3$ ligand weakens the σ bond of the water molecule coordinated *trans* to it. At the same time the π acidity of the phosphite decreases as its σ basicity increases, making the d_π electrons of the Ru(II) center more available to the formation of the outer-sphere complex with isn in the activated complex.

The possibility of a correlation between K_{os}, the outer sphere association constant [4], and k_1 will be of interest:

$$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+} + isn \xrightarrow{K_{os}} \{[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}\cdot isn\}$$

A trend could be observed: k_1 increases as K_{os} increases in the series (K_{os} = 0.9, 0.5, 0.4, 1.5 and 4.3 for Me, Et, Pr, ^{i}Pr and Bu, respectively); but the changes are too small to justify speculation.

As pointed out earlier [4, 15], the formal potential $E^{o\prime}$ for the couple Ru(II)/Ru(III) in monophosphite complexes *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ reflects the electronic effects in stabilizing Ru(II) relative to Ru(III). The $E^{o\prime}$ data are +0.74, +0.70, +0.68, +0.67, and +0.66 V (*vs.* N.H.E.) for R = Me, Et, Pr, Bu and ^iPr, respectively.

Again, a connection can be observed between the availability of the d_π electrons of the Ru(II) center and the k_1 data. As the $E^{o\prime}$ becomes less positive, the d_π electrons of the metal center are more available for outer-sphere complex formation, making the substitution of the water molecule easier.

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

The specific rate k_1 was evaluated from the limiting slope and k_{-1} from the intercept. The activation parameters were evaluated from the Eyring equation. Equilibrium constants and thermodynamic parameters were calculated from the rate constants.

The outer-sphere association constants, K_{os}, of *trans*-$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}$ with isn were calculated [4] from the following scheme:

$$[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+} + isn \xrightarrow{K_{os}} \{[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}\cdot isn\}$$

$$\{[Ru(NH_3)_4P(OR)_3(H_2O)]^{2+}\cdot isn\} \underset{k_{-1}'}{\overset{k_1'}{\rightleftarrows}} [Ru(NH_3)_4P(OR)_3isn]^{2+} + H_2O$$

Under pseudo-first-order conditions, isn in excess, is governed by

$$k_{obs} = \frac{k_1' K_{os}[isn]}{K_{os}[isn] + 1} + k_{-1}'$$

or

$$\frac{1}{k_{obs} - k_{-1}'} = \frac{1}{k_1'} + \frac{1}{k_1' K_{os}[isn]}$$

The values of k_{-1}, are the intercepts in plots of k_{obs} *vs.* [isn]; from the plots of $1/(k_{obs} - k_{-1}')$ *vs.* 1/[isn], k_1' and K_{os} can be evaluated.

As the $\Delta H_1^{\neq}$ and $\Delta H_{-1}^{\neq}$ may be related mainly to electronic effects and the $\Delta S_1^{\neq}$ and $\Delta S_{-1}^{\neq}$ data may account for the environmental effects [16], the changes on $\Delta S_1^{\neq}$ and $\Delta S_{-1}^{\neq}$ observed for butyl and isopropyl complexes with respect to the other phosphites reflect their steric hindrance and the hydrophobic character of the phosphorus moiety.

Although the ligands dealt with in this work are not bulky molecules, it is expected that the size of phosphites has some influence on rates and equilibria. The rates of substitution of the coordinated water molecule k_{-1} increase as the cone angle [17] of R increases: Me < Et ~ Pr ~ Bu < ^iPr. The rates for the isn aquation, k_{-1}, exhibit similar behavior, with an inversion for ^iPr: Me < Et < Pr < Bu < ^iPr. It is not surprising that steric hindrance increases the rate of dissociation of the ligand *trans* to the phosphorus. These are speculative considerations since synergism between the σ and π components of the P(III)–Ru(II)–isn bonds is operative and works at the same time as the steric effects. The electronic and environmental effects may work in the same direction or independently for the particular ligand. More data are required for a complete analysis of how *trans*-labilizing groups produce the effects they do. Work in this direction is currently in progress in our laboratory and will be reported later.

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