distance is 1.260 (6) Å. Unfortunately, structural parameters for the uncoordinated ligand are not available; however, the corresponding distances in $UO_2[Ph_2P(O)CH_2C(O)NEt_2](NO_3)_2$ are known: P–O = 1.512 (5) Å and C–O = 1.264 (8) Å. The slightly shorter P–O distance in **3** suggests that there is a smaller degree of electron transfer from the phosphoryl P–O bond to the Nd ion in **3**, which would be consistent with a weaker Nd–OP interaction.

At the level of accuracy of this structure determination no unusual structural features in the inner coordination sphere are revealed. In addition, no unusual intramolecular nonbonded distances or steric perturbations are found that could be responsible for the "aryl strengthening" effect. Apparently, factors that lead to the enhanced extraction ability of phenyl-substituted CMP ligands at high acid concentrations are not revealed in this solid-state structure analysis.

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Supplementary Material Available: Listings of structure factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen atom positional and thermal parameters (26 pages). Ordering information is given on any current masthead page.

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Synthesis and Properties of the Ruthenium(II) Complexes *cis*-$Ru(NH_3)_4(isn)L^{2+}$. Spectra and Reduction Potentials

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In an earlier paper,[2] the synthesis and photochemical properties of trans-disubstituted tetraammineruthenium(II) complexes, *trans*-$Ru(NH_3)_4LL'^{2+}$ (where L and L′ each are substituted pyridines) were reported. In order to extend the study we decided to examine the analogous cis system. Although the *cis*-dipyridyltetraammine complex *cis*-$Ru(NH_3)_4(py)_2{}^{2+}$ is known, examples of hetero bis-substituted complexes have not been previously isolated and characterized. However, rate[3,4] and cyclic voltammetry[5] studies indicate that the synthesis of the *cis*-tetraammineruthenium(II) complexes should be quite feasible. Described here are the synthesis and characterization of the *cis*-tetraammineruthenium(II) complexes *cis*-$Ru(NH_3)_4(isn)L^{2+}$, for which L = pyridine (py), 4-picoline (4-pic), isonicotinamide (isn), pyrazine (pz), or 4-acetylpyridine(4-acpy).

Experimental Section

Chemicals and Reagents. Ruthenium trichloride ($RuCl_3 \cdot 3H_2O$) (Strem) was the starting material for ruthenium complexes synthesis. Pyrazine (pz) (99.9%, Aldrich Gold Label) was used as supplied. Isonicotinamide (isn) (Aldrich) was recrystallized from water before use. 4-Picoline (4-pic) (Aldrich) and 4-acetylpyridine (4-acpy) were distilled before use. Sodium tetrafluoroborate ($NaBF_4$) was recrystallized from water. Ether, ethanol, and acetone were purified before use. Doubly distilled water was used throughout this work. All other chemicals were reagent grade and were used as supplied.

Ruthenium Complexes. *cis*-$[Ru(NH_3)_4(isn)Cl]Cl_2$ was prepared by following the literature procedure.[5]

cis-$[Ru(NH_3)_4(isn)L](BF_4)_2$ complexes were prepared by adapting the method described to prepare $[Ru(NH_3)_5L](BF_4)_2$[6] and *trans*-$[Ru(NH_3)_4LL'](BF_4)_2$.[2] A 100-mg (0.25-mmol) sample of *cis*-$[Ru(NH_3)_4(isn)Cl]Cl_2$ was dissolved in ~1.5 mL of water and deaerated with argon. Trifluoroacetic acid (TFA) (1 drop) and Zn(Hg) (~0.5 g) were then added, and the reaction was allowed to proceed for about 20 min with continuous argon bubbling. The resulting red solution was transferred under argon to a large excess of the ligand L. After 2 h of reaction time in the dark, the resulting solution was filtered and to it was added about 1 mL of a freshly prepared, deaerated, and almost saturated solution of $NaBF_4$ (~1 g/mL). After the mixture was cooled, the precipitate was collected by filtration, washed with ethanol and ether, and air-dried. The compounds were recrystallized several times in order to obtain analytically pure compounds. Recrystallizations were performed by dissolving the compounds in ~0.5–1.0 mL of warm deaerated water (~40 °C), filtering, and cooling in an ice bath. The precipitate was collected by filtration, washed, and dried as before. Prior to recrystallization, excess unreacted pyrazine in *cis*-$[Ru(NH_3)_4(isn)(pz)](BF_4)_2$ was eliminated by extraction with warm ethanol (~45 °C), which was done by suspending the crude compound in ethanol and then filtering.

Analysis. Carbon, hydrogen, and nitrogen microanalyses were performed by the staff of Dr. Riva M. Cruz of the Instituto de Química da Universidade de São Paulo.

Anal. Calcd for L = C_6H_7N: C, 25.8; N, 17.6; H, 4.5. Found: C, 25.8; N, 17.5; H, 4.3. Calcd for L = C_5H_5N: C, 24.3; N, 18.1; H, 4.3. Found: C, 24.6; N, 18.7; H, 4.2. Calcd for L = $C_6H_6N_2O$: C, 24.5; N, 19.1; H, 4.1. Found: C, 22.6; N, 18.8; H, 4.0. Calcd for L = C_7H_7NO: C, 26.6; N, 16.7; H, 4.3. Found: C, 27.2; N, 16.3; H, 4.3. Calcd for L = $C_4H_4N_2$: C, 22.0; N, 20.6; H, 4.1. Found: C, 22.4; N, 20.9; H, 4.2.

Cyclic Voltammetry. The cyclic voltammograms of the complexes were taken with a PARC electrochemical system consisting of a Model 175 universal programmer, a Model 173 potentiostat-galvanostat, and a RE 0074 X-Y Recorder, and with a CV-1B Cyclic Voltammograph from Bio-Analytical Systems and a Omnigraphic 100 X-Y Recorder from Houston Instrument. Scan rates of 20, 50, 100, 200, 300, 400, and 500 mV/s were employed. The electrochemical cells used were of the three-electrode type with Ag/AgCl in saturated potassium chloride solution as a reference electrode and platinum wire as an auxiliary electrode. The working electrode was a glassy-carbon electrode. All electrochemical data were obtained in supporting electrolyte solutions of 0.10 M ionic strength at 25 °C prepared from TFA and NaTFA at pH 3, and with millimolar concentrations of the complex. All solutions were deaerated with argon prior to the electrochemical measurements. The formal reduction potentials were calculated as the arithmetic mean of the anodic and cathodic peak potentials. E_f values were converted to NHE by adding 0.199 V.

Spectra. Electronic spectra were recorded at room temperature with a Beckman UV-5270 or a Varian 634-S recording spectrophotometer using quartz cells. Solutions used to measure extinction coefficients were prepared gravimetrically with quantitative dilution.

pK_a Determinations. A stock solution of the complex in water was used. The desired series of solutions with different acid (HCl) concentrations were obtained by dilution of measured volumes of the stock solutions of the complex and of HCl. The ionic strength (μ) was fixed at 1.0 M with sodium chloride. The pK_a values were determined by using the method described previously,[6,7] where log $(A_{\lambda_1}/A_{\lambda_2})$ is plotted against pH and λ_1 and λ_2 represent absorption maxima for the unprotonated (B) and protonated (BH^+) forms, respectively. The pK_a corresponds to the pH where log $(A_{\lambda_1}/A_{\lambda_2})$ equals log $(\epsilon(B)_{\lambda_1} + \epsilon(BH^+)_{\lambda_1})/(\epsilon(B)_{\lambda_2} + \epsilon(BH^+)_{\lambda_2})$. The reported pK_a is average of three independent determinations.

Results and Discussion

Synthesis. The synthesis of the cis isomers of bis hetero-substituted ruthenium(II) tetraammines described here use the previously reported[5] *cis*-$[Ru(NH_3)_4(isn)Cl]Cl_2$ as the starting complex. From this point, the method used for the synthesis of ruthenium(II) pentaammines[6] was adapted for this case. In the synthetic paths were considered the stereoretentive substitution behavior of ruthenium(II) ammine-substitution reactions,[8] the

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Table I. Electronic Spectra of *cis*-$Ru(NH_3)_4(isn)L^{n+}$ Complexes and Analogous *cis*-$Ru(NH_3)_4L_2^{n+}$ and $Ru(NH_3)_5L^{n+}$ Complexes in Aqueous Solutions[a]

complex	ν_{max} (log ϵ)[b] MLCT-1	MLCT-2	IL (intraligand bands)
cis-$Ru(NH_3)_4(isn)(4\text{-pic})^{2+}$	467 (4.05)	371 (3.85)	246 (3.87), 257 sh
cis-$Ru(NH_3)_4(isn)(py)^{2+}$	466 (4.01)	378 (3.83)	247 (3.90), 257 sh
cis-$Ru(NH_3)_4(isn)(4\text{-acpy})^{2+}$	503 (4.13)	426 (4.02)	262 (3.81), 218 sh
cis-$Ru(NH_3)_4(isn)_2^{2+}$	478 (4.13)	413 (4.01)	257 (3.88)
cis-$Ru(NH_3)_4(isn)(pz)^{2+}$	476 (4.14)	405 (3.98)	257 (4.05)
cis-$Ru(NH_3)_4(isn)(pzH)^{3+}$[c]	547 (4.20)	375 (3.78)	270 (3.94)
$Ru(NH_3)_5(py)^{2+}$[d]	407 (3.89)		244 (3.66)
$Ru(NH_3)_5(4\text{-acpy})^{2+}$[e]	523 (3.97)		271 (3.53), 223 (3.76)
$Ru(NH_3)_5(pz)^{2+}$[e]	472 (4.03)		253 (3.78)
$Ru(NH_3)_5(pzH)^{3+}$[e]	529 (4.08)		272 (3.81)
$Ru(NH_3)_5(isn)^{2+}$[f]	479 (4.06)		260 (3.66)
$Ru(NH_3)_5(4\text{-pic})^{2+}$[d]	397 (3.89)		244 (3.66)

[a] In dilute aqueous solution except where noted; BF_4^- salts in each case. [b] ν_{max} in nm; ϵ is the molar extinction coefficient. [c] In 0.75 N aqueous HCl (μ = 1 M $H^+,Na^+/Cl^-$). [d] Reference 6. [e] Reference 10. Malouf, G. Ph.D. Dissertation, University of California, Santa Barbara, CA, 1977. [f] Reference 11.

relative lability of aquo and chloride ligands when coordinated to Ru(II), and the Ru(II) preference for unsaturated ligands.[9] Thus, reduction of slightly acidic solutions of *cis*-$[Ru(NH_3)_4(isn)Cl]Cl_2$ with Zn(Hg) yields *cis*-$Ru(NH_3)_4(isn)(H_2O)^{2+}$, which, in the presence of excess L, produces *cis*-$Ru(NH_3)_4(isn)L^{2+}$, according to the following general scheme:

$$cis\text{-}Ru^{III}(NH_3)_4(isn)Cl^{2+} + H_2O \xrightarrow[Zn(Hg)]{Ar,\ H^+} cis\text{-}Ru^{II}(NH_3)_4(isn)(H_2O)^{2+} + Cl^- \xrightarrow{excess\ L'} cis\text{-}Ru^{II}(NH_3)_4(isn)L^{2+}$$

the synthesis of such compounds shows that the ring systems do not pose major steric barriers, as previously inferred.[5]

Spectra of Ruthenium(II) Complexes. The electronic spectra of the *cis*-$Ru(NH_3)_4(isn)L^{2+}$ complexes synthesized, along with those of related complexes, are summarized in Table I.

The strong absorption bands in the UV region are similar in intensity and position to bands observed in spectra of the free ligands[6] and can be assigned as intraligand π–π^* (IL) in character. The electronic spectra of these complexes are dominated in the visible region by two very intense absorption bands (ϵ varying in the vicinity of 10^4 M^{-1} cm^{-1}) (Figure 1), with the more intense band being the lower in energy. These two bands are assigned as metal-to-ligand charge-transfer (MLCT) transitions in analogy to spectral assignments[8,12] of similar absorptions in the homo disubstituted ions *cis*-$Ru(NH_3)_4L_2^{2+}$ (L = py, pz, or isn). The complex *cis*-$Ru(NH_3)_4(isn)L^{2+}$ can also be considered as a $Ru(NH_3)_4(isn)^{2+}$ core to which a ligand was added in a cis position. Thus, a shift to higher or lower energy, in *cis*-$Ru(NH_3)_4(isn)L^{2+}$ spectra, can be interpreted as reflecting, respectively, the electron-releasing or electron-withdrawing character of the substituents on the L ligand, as is the case in $Ru(NH_3)_5L^{2+}$,[10] as evidenced by the red shift of MLCT-1 upon protonation of the cis isonicotinamide pyrazine complex (Figure 1). However, the energy of the MLCT-2 band seems more sensitive to the nature of the sixth ligand. Inspection of Table I shows that the order of energies of the MLCT-2 bands and the correspondent MLCT bands in $Ru(NH_3)_5L^{2+}$ is the same.

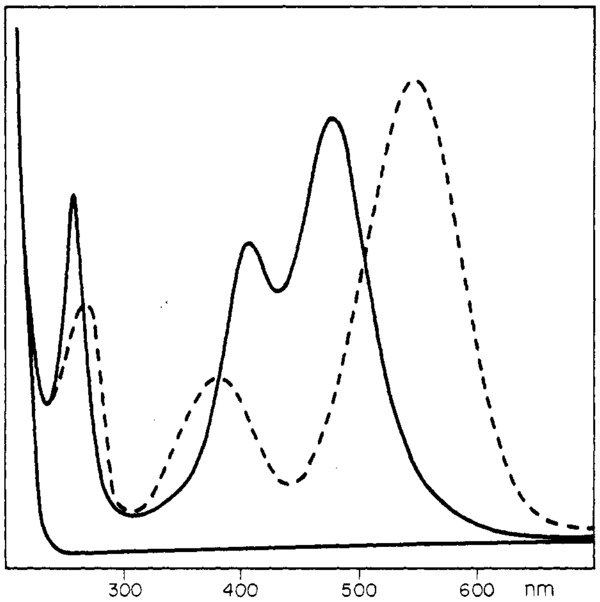
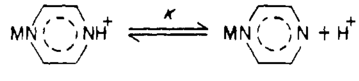


Figure 1. Spectra in aqueous solutions of *cis*-$Ru(NH_3)_4(isn)(pz)^{2+}$ and *cis*-$Ru(NH_3)_4(isn)(pzH)^{3+}$: (—) *cis*-$Ru(NH_3)_4(isn)(pz)^{2+}$ in dilute aqueous solution; (--) *cis*-$Ru(NH_3)_4(isn)(pzH)^{3+}$ in 1 M HCl.

pK_a of Coordinated Pyrazine. The marked changes in the absorption spectra of the ruthenium(II) pyrazine complex upon protonation of the remote pyrazine nitrogen (Figure 1) allow evaluation of complex pK_a[6,7] (–log *k* for eq 1) by using similar



(1)

M = *cis*-$Ru(NH_3)_4(isn)^{2+}$

experimental procedures and data treatment as previously reported.[2] Upon protonation, band maxima of *cis*-$Ru(NH_3)_4(isn)(pz)^{2+}$ were shifted to 547 nm (ϵ = 16000 M^{-1} cm^{-1}), 375 nm (ϵ = 6000 M^{-1} cm^{-1}), and 270 nm (ϵ = 8700 M^{-1} cm^{-1}), with isosbestic points at 507 and 382 nm. The pK_a of *cis*-$Ru(NH_3)_4(isn)(pz)^{2+}$ so determined is 1.7 at 25 °C.

Previous studies with $Ru(NH_3)_5(pz)^{n+}$[6] and *trans*-$Ru(NH_3)_4L(pz)^{n+}$[2] complexes showed that the decreased acidity of the Ru(II)-coordinated pzH^+ relative to that of the free ligand could be attributed to π back-bonding delocalizing electron density from the Ru(II) center into the π^* orbitals of the nitrogen heterocycle and, furthermore, that the effect of the trans ligand L, in *trans*-$Ru(NH_3)_4L(pz)^{n+}$, on the acidity of Ru(II)-coordinated pzH^+ follows the order of increasing acidity with both decreasing σ-donor and increasing π-acceptor strengths of the trans L group.[2] Thus, in *cis*-$Ru(NH_3)_4(isn)(pz)^{2+}$, the pK_a of 1.7 indicates that the acidity of the coordinated pz is decreased by about 1 order of magnitude relative to the free ligand (pK_a 0.65), and its acidity is increased when compared with the pK_a of $Ru(NH_3)_5(pz)^{2+}$ (2.5), and lies in between those of *trans*-$Ru(NH_3)_4(py)(pz)^{2+}$ (2.0) and *trans*-$Ru(NH_3)_4(pz)_2^{2+}$ (1.5). The effect of the substitution of a cis ammonia by isonicotinamide, a ligand with lower σ-donor and higher π-acceptor ability than ammonia, would be to further release electron density from the ruthenium center and thus increase the Ru(II)-coordinated pz acidity relative to that of $Ru(NH_3)_5(pz)^{2+}$.

Reduction Potentials. Formal reduction potentials of *cis*-$Ru(NH_3)_4(isn)L^{3+}$ by the cyclic voltammetry technique are listed in Table II. The CV values of each complex fit most of the criteria employed.[13] A CV of the reversible $Ru(NH_3)_5(py)^{2+}$ was run under the same conditions, and its values were used for comparison. Peak to peak separations increased (from 50 to 80 mV) with increasing scan rate (from 20 to 500 mV), which might be due

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Table II. Formal Reduction Potentials of Ruthenium Complexes

redox couples	E_f[a]	medium	ref
$Ru(NH_3)_5(py)^{3+/2+}$	0.289	*f*	this work
	0.298	*b*	15
	0.300	*b*	16
	0.305	*c*	14
	0.350	*c*	17
	0.420	*d*	11
$Ru(NH_3)_5(isn)^{3+/2+}$	0.375	*b*	15
	0.440	*d*	11
$Ru(NH_3)_5(4\text{-}acpy)^{3+/2+}$	0.392	*b*	15
$Ru(NH_3)_5(pz)^{3+/2+}$	0.490	*e*	14
cis-$Ru(NH_3)_4(4\text{-}pic)(isn)^{3+/2+}$	0.539	*f*	this work
cis-$Ru(NH_3)_4(isn)(py)^{3+/2+}$	0.576	*f*	this work
cis-$Ru(NH_3)_4(isn)(pz)^{3+/2+}$	0.754	*f*	this work
cis-$Ru(NH_3)_4(isn)(4\text{-}acpy)^{3+/2+}$	0.656	*f*	this work
cis-$Ru(NH_3)_4(isn)_2{}^{3+/2+}$	0.654	*f*	this work
	0.700	*d*	11
cis-$Ru(NH_3)_4(py)_2{}^{3+/2+}$	0.505	*b*	15
cis-$Ru(NH_3)_4(pz)_2{}^{3+/2+}$	0.860	*e*	14
$(NH_3)_5Ru(pz)Ru(NH_3)_5{}^{5+/4+}$	0.350	*e*	14
	0.400	*e*	18
$(NH_3)_5Ru(pz)Ru(NH_3)_5{}^{6+/5+}$	0.740	*e*	14
	0.760	*e*	18

[a] In volts vs. the NHE; all new values reported are ±0.010 V as obtained from reversible waves from cyclic voltammetry. [b] At 25 °C, complex is $\sim 1 \times 10^{-3}$ M in an aqueous solution of 0.10 M p-toluenesulfonic acid/0.10 M potassium *p*-toluenesulfonate. [c] Aqueous solution of 0.1 M CF_3CO_2H/0.1 M $CF_3CO_2{}^-Na^+$; by cyclic voltammetry. [d] Measured from the potential of an equimolar Ru(II)/Ru(III) solution at a platinum electrode vs. a silver wire in 1.00 M KCl/0.001 M HCl. [e] 1 M NaCl. [f] At 25 °C, complex is $\sim 1 \times 10^{-3}$ M in an aqueous solution of 1×10^{-3} M CF_3CO_2H/0.1 M $CF_3CO_2{}^-Na^+$; by cyclic voltammetry.

to cell resistance. Some differences in the values of formal reduction potentials appeared in the literature (Table II), and in some cases they were eventually attributed to different experimental conditions.[14] There is a difference between the new value listed and the previous one measured by a potentiometric technique for the *cis*-$Ru(NH_3)_4(isn)_2{}^{3+}$ complex.[11] However, an inspection of the formal reduction potentials in Table II for py and isn pentaammine complexes shows that E_f values measured by CV are about 65–131 mV smaller than those reported in ref 11, which were obtained by potentiometry. In this case, the E_f value here reported for *cis*-$Ru(NH_3)_4(isn)_2{}^{3+}$ is 46 mV smaller than the previously reported one,[11] measured by potentiometry.

Previous observations showed that π-unsaturated ligands, such as pyridines (py–X), lead to substantially more positive reduction potentials for the $Ru(NH_3)_5{}^{3+/2+}$ couples than when L is H_2O or NH_3, and that the electron-withdrawing substituents (X) increase E_f; that is, the π-accepting ability of the ligands (or in other words, π back-bonding) increases E_f values.[15] It was also observed[14] that the effect on E_f of the substitution of a second ammonia by another ligand to give a *cis*-$Ru(NH_3)_4L_2{}^{3+/2+}$ (L = isn, 4-acpy, pz, py) complex appeared to be additive (Table II), thus yielding more positive E_f values than for the corresponding $Ru(NH_3)_5L^{3+/2+}$. Similarly, when an ammonia of $Ru(NH_3)_5(isn)^{3+/2+}$ is substituted by another ligand L to yield *cis*-$Ru(NH_3)_4(isn)L^{3+/2+}$, more positive E_f values are also obtained. This is expected since another π-acceptor ligand, with weaker σ-donor strength, is being added, favoring the stabilization of Ru(II) relative to Ru(III). For *cis*-$Ru(NH_3)_4(isn)L^{3+/2+}$, the more positive E_f values are obtained with ligands L of higher π-acceptor and lower σ-donor abilities, and this order is the same as that observed in $Ru(NH_3)_5L^{3+/2+}$.[15] However, ΔE_f from $Ru(NH_3)_5L^{3+/2+}$ to *cis*-$Ru(NH_3)_4L_2{}^{3+/2+}$ varies depending on L, from ~210 mV for L = py to ~370 mV for L = pz. Now, if the series *cis*-$Ru(NH_3)_4(isn)L^{3+/2+}$ and $Ru(NH_3)_5L^{3+/2+}$ is considered, ΔE_f is almost the same, ranging from 264 to 287 mV (Table II). This might be considered as the contribution of isn to the E_f value of *cis*-$Ru(NH_3)_4(isn)L^{3+/2+}$, when isn substitutes one cis ammonia in $Ru(NH_3)_5L^{3+/2+}$. In analyzing the charge-transfer spectra of *cis*-$Ru(NH_3)_4L_2{}^{2+}$ by means of molecular orbital theory, Zwickel and Creutz[12] assumed that the rings in the cis system were oriented in the *xz* and *yz* planes of the octahedron. However, the similar contributions of isn for E_f values in *cis*-$Ru(NH_3)_4(isn)L^{2+}$, if not by chance or due to more complex factors, imply that the contributions of isn and L are independent, suggesting that each ligand interacts with a different d_π metal orbital in these complexes, and thus, the rings could not be oriented in the *xz* and *yz* planes of the octahedron. As a matter of fact, the crystal structure of one of these compounds, namely *cis*-$Ru(NH_3)_4(isn)_2{}^{2+}$, indicates that the dihedral angles of the rings are 51.4 and 52.8°.[19] Thus, for the cis system, the molecular orbital treatment should then consider four orbitals, two d_π metal (two out of the three linear combinations of the t_{2g} orbitals) and two ligand orbitals. Accordingly, the absorption spectra of *cis*-$Ru(NH_3)_4(isn)L^{2+}$ and *cis*-$Ru(NH_3)_4L_2{}^{2+}$ would still be expected to display two MLCT bands, as is the case.

Lastly, in order to further examine the CV and spectral properties of the ruthenium(II) tetraammines, the *cis*-$Ru(NH_3)_4LL'^{2+}$ and *trans*-$Ru(NH_3)_4LL'^{2+}$ systems are being investigated in this laboratory.

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Registry No. *cis*-$[Ru(NH_3)_4(isn)(4\text{-}pic)](BF_4)_2$, 98858-88-9; *cis*-$[Ru(NH_3)_4(isn)(py)](BF_4)_2$, 98858-89-0; *cis*-$[Ru(NH_3)_4(isn)(4\text{-}acpy)](BF_4)_2$, 98858-91-4; *cis*-$[Ru(NH_3)_4(isn)_2](BF_4)_2$, 98858-92-5; *cis*-$[Ru(NH_3)_4(isn)(pz)](BF_4)_2$, 98858-94-7; *cis*-$[Ru(NH_3)_4(isn)(pzH)](BF_4)_3$, 98858-95-8; *cis*-$Ru(NH_3)_4(isn)(4\text{-}pic)^{3+}$, 98858-96-9; *cis*-$Ru(NH_3)_4(isn)(py)^{3+}$, 98858-97-0; *cis*-$Ru(NH_3)_4(isn)(pz)^{3+}$, 98858-98-1; *cis*-$Ru(NH_3)_4(isn)(4\text{-}acpy)^{3+}$, 98858-99-2; *cis*-$Ru(NH_3)_4(isn)_2{}^{3+}$, 50573-22-3; *cis*-$[Ru(NH_3)_4(isn)Cl]Cl_2$, 63323-69-3; $Ru(NH_3)_5(py)^{2+}$, 21360-09-8; $Ru(NH_3)_5(py)^{3+}$, 33291-25-7; pz, 290-37-9.

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