bands to Pt-P stretching modes is probably incorrect. As previously suggested, they are more likely internal ligand modes split or activated by complexation.[2,27-29] In fact, most of the bands in the far infrared and Raman spectra of the complexes studied can be correlated very well with vibrations of free Ph_3P,[27,28] both in position and relative intensity. However, there are bands in the 160-200-cm^{-1} region of the spectra of all complexes studied (weak in the infrared and strong in the Raman) which do not appear in the spectra of the free ligand. There are two such bands between 195 and 170 cm^{-1} in the spectra of the cis complexes and one band, at 165-175 cm^{-1}, in the spectra of the trans (Figure 2). We tentatively assign these bands as the Pt(II)-P stretching modes (see Table I). This assignment is consistent with those recently made by use of the metal isotope technique for Ni(II)-Ph_3P and Pd(II)-Ph_3P stretching frequencies[29] and with assignments of M-Ph_3P stretching modes for a variety of other metals.[30]

Unfortunately, the 160-200-cm^{-1} region of the infrared is not generally accessible and therefore these bands are not particularly useful for the assignment of geometries on a routine basis. However, the intensity of a band at 550 ± 5 cm^{-1} in the infrared and Raman spectra of all complexes studied also appears to depend on complex stereochemistry. The origin of this band is uncertain, but it is possibly the weak infrared-active 540-cm^{-1} band of Ph_3P itself (Figure 1a), assigned as the first overtone of the asymmetric PC_3 deformation mode,[27] which has undergone a typical 10-cm^{-1} shift to higher frequency on complexation.[2] In any event, this band, starred in Figures 1 and 3, is very strong (using the ligand vibrations at *ca.* 500 and 420-450 cm^{-1} as internal standards for intensity comparison) in the infrared of cis complexes and weak in the infrared of trans. Conversely, this band is very weak (using the band at *ca.* 620 cm^{-1} for comparison) in the Raman of cis complexes and very strong in the Raman of trans. We therefore propose the use of the intensity of this band as a simple criterion for the assignment of stereochemistry in $Pt(Ph_3P)_2XY$ type complexes.

Acknowledgments. Support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We are also indebted to Professor Kazuo Nakamoto for providing far infrared facilities and to Ms. Doris Stogsdill and Mr. Charles E. Scott of Monsanto Co. for elemental and thermogravimetric analyses.

Registry No. *cis*-$Pt(Ph_3P)_2Cl_2$, 15604-36-1; *trans*-$Pt(Ph_3P)_2Cl_2$, 14056-88-3; *cis*-$Pt(Ph_3P)_2Br_2$, 18517-48-1; *trans*-$Pt(Ph_3P)_2Br_2$, 26026-46-0; *cis*-$Pt(Ph_3P)_2I_2$, 35085-00-8; *trans*-$Pt(Ph_3P)_2I_2$, 35085-01-9; $Pt(Ph_3P)_2O_2$, 15614-67-2; *trans*-$Pt(Ph_3P)_2Cl(CO_2Me)$, 20524-02-1; *trans*-$Pt(Ph_3P)_2HCl$, 16841-99-9.

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Chromium(II)-Catalyzed Aquation of a Bridged Ruthenium(II)-Chromium(III) Complex Ion

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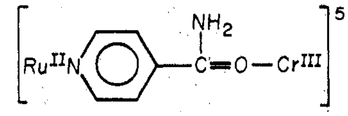
The reaction of isonicotinamidepentaammineruthenium(III) with chromium(II) in LiBr-HBr media has been shown to produce only



I

which in the presence of excess ruthenium(III) undergoes a slow aquation reaction to form isonicotinamidepentaammineruthenium(II) and chromium(III).[1] The present report describes our studies of the chromium(II)-catalyzed aquation of I in $LiClO_4$-$HClO_4$ media.

Experimental Section

Reagents. Tap distilled water was redistilled from alkaline potassium permanganate before being used in kinetic experiments. All chemicals used were of reagent grade or better. Lithium perchlorate from G. F. Smith Co. was prereduced with chromium(II) and then recrystallized from water twice before use. A stock solution of hexaaquochromium(III) was prepared by the reduction of primary standard potassium dichromate with hydrogen peroxide in the presence of excess perchloric acid and was standardized titrimetrically[2] and spectrophotometrically.[3] Chromium(II) perchlorate solutions were prepared by reducing solutions of chromium(III) perchlorate over freshly prepared zinc amalgam under a blanket of argon gas. Isonicotinamidepentaammineruthenium(III) perchlorate was prepared as previously described.[1]

Kinetic Measurements. Solutions of the reactants were prepared and mixed using an all-glass apparatus composed of a Zwickel flask[4] to which was attached a 10-ml buret fitted at the top with a Cr^{2+} preparation flask. The Zwickel flask was immersed in a constant temperature bath. Pressure from the blanketing gas argon was used to transfer the reaction mixtures to a 1.0-cm cell. The aquation reaction was followed at 540 nm, a wavelength of maximum difference in molar absorptivity between I and isonicotinamidepentaammineruthenium(II), using a Cary Model 17I recording spectrophotometer equipped with a thermostated cell compartment. Reaction conditions were always pseudo first order with the first-order rate constant, k_{obsd}, being obtained from the slope of a plot of log $(A_t - A_\infty)$ *vs.* time, where A_t is the absorbance at time t and A_∞ is the theoretical absorbance after the reaction is complete assuming isonicotinamidepentaammineruthenium(II) as the final product. A nonlinear least-squares computer program written by Lietzke[5] was used in analyzing the $[Cr^{2+}]$ and $[H^+]$ dependence of the rate of the aquation reaction. Values of the rate constants k_0, k_1, and k_2 reported are weighted averages[6] based upon the values and the error limits of the slopes and intercepts of the computer-fitted data.

Results and Discussion

The slow spontaneous aquation of I has been studied by Gaunder and Taube[1] in LiBr-HBr media. The reaction in $LiClO_4$-$HClO_4$ media was found to be accompanied by

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Table I. Observed Rate Constants for the Aquation of I in the Presence of Excess Chromium(II)[a]

10^5[I], *M*	$10^3 \times$ $[Cr^{2+}]_{excess}$, *M*	$[H^+]$, *M*	$10^5 k_{obsd}$, sec^{-1}	μ
6.94	4.60	0.100	2.79	1.0
7.64	4.60	0.400	0.933	1.0
8.39	4.60	0.800	0.652	1.0
6.97	9.29	0.100	4.95	1.0
7.80	9.29	0.400	1.28	1.0
7.40	9.29	0.800	0.991	1.0
9.78	14.1	0.100	7.30	1.0
7.45	14.1	0.125	6.20	1.0
7.87	14.1	0.400	1.99	1.0
7.73	14.1	0.800	1.07	1.0
8.50	16.1	0.100	8.20	1.0
7.83	16.1	0.300	2.73	1.0
7.23	16.1	0.500	1.68	1.0
11.3	2.0	0.100	0.948	0.40
10.2	2.42	0.100	0.263	0.40
12.3	7.85	0.100	2.85	0.40
8.10	10.0	0.100	3.81	0.40
6.62	15.1	0.100	5.44	0.40
7.04	13.1	0.0792	5.76	0.40
5.34	13.1	0.100	4.85	0.40
4.70	13.1	0.123	3.98	0.40
6.68	13.1	0.131	3.62	0.40
7.35	13.1	0.246	1.95	0.40
7.77	13.1	0.323	1.66	0.40
8.10	10.0	0.116	3.21	0.40
7.32	10.0	0.136	2.83	0.40
5.89	10.0	0.166	2.30	0.40
6.60	10.0	0.196	1.89	0.40

[a] All experiments are at 25°.

oxidation of ruthenium(II)-containing species by the perchloric acid. The aquation in LiBr-HBr media was shown to obey the rate law

$$\frac{-d[I]}{dt} = \left(k_0 + \frac{k_1}{[H^+]}\right)[I] \qquad (1)$$

where $k_0 = 1.02 \times 10^{-5}$ sec^{-1} and $k_1 = 8.4 \times 10^{-8}$ *M* sec^{-1} at 25.0° and $\mu = 0.10$.

The presence of excess Cr^{2+} accelerates the rate of aquation of I; however, the kinetics of the Cr^{2+}-catalyzed reaction are complicated by the presence of bromide ion. In particular after the initial rapid formation of I in the presence of Br^- and excess Cr^{2+}, the absorbance at 550 nm, a wavelength of maximum difference in molar absorptivity between I and isonicotinamidepentaammineruthenium(II), slowly rises over a period of about 1 hr and then decreases. In $LiClO_4$-$HClO_4$ media the absorbance changes described above are not observed. At the concentrations of excess Cr^{2+} used in these experiments ((4.60-16.1) $\times 10^{-3}$ *M*) the kinetics of the aquation of I are not complicated by the slower perchloric acid oxidation of ruthenium(II)-containing species at least throughout 1 half-life of the reaction.

The results of the kinetics experiments for the Cr^{2+}-catalyzed aquation of I are summarized in Table I. Plots of k_{obsd} *vs.* $[Cr^{2+}]$ at fixed $[H^+]$ shown in Figure 1 and of k_{obsd} *vs.* $[H^+]^{-1}$ at fixed $[Cr^{2+}]$ shown in Figure 2 indicate that there are at least three pathways for the aquation of I which are described by the rate law

$$\frac{-d[I]}{dt} = \left(k_0 + \frac{k_1}{[H^+]} + \frac{k_2[Cr^{2+}]}{[H^+]}\right)[I] \qquad (2)$$

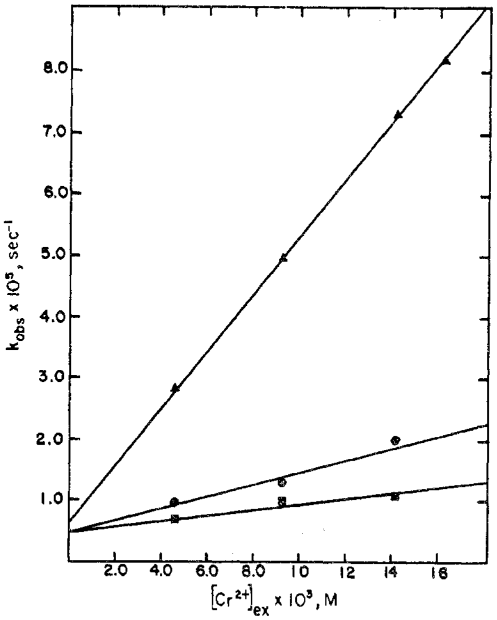


Figure 1. Plot of k_{obsd} for the aquation of I *vs.* $[Cr^{2+}]$: triangles, at 0.10 *M* H^+; dots, at 0.40 *M* H^+; squares, at 0.80 *M* H^+.

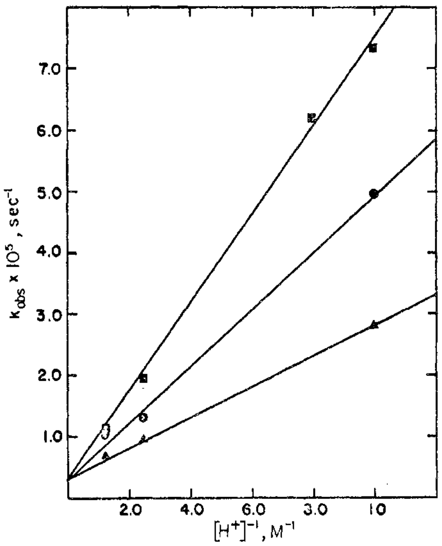


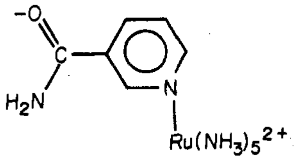
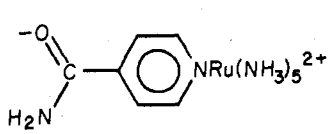
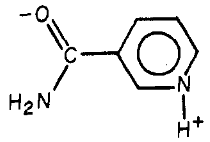
Figure 2. Plot of k_{obsd} for the aquation of I *vs.* $[H^+]^{-1}$: squares, at 0.0141 *M* Cr^{2+}; dots, at 0.0093 *M* Cr^{2+}; triangles, at 0.0046 *M* Cr^{2+}.

Table II. Temperature Dependence Data for the Cr^{2+}-Catalyzed Aquation of *I* at $\mu = 0.40$

10^5[I], *M*	$10^3 \times$ $[Cr^{2+}]$, *M*	$[H^+]$, *M*	$10^5 k_{obsd}$, sec^{-1}	Temp, °C
5.70	10.0	0.136	0.849	15.5
7.32	10.0	0.136	2.83	25.3
6.76	10.0	0.136	9.74	35.4
6.61	10.0	0.136	24.5	41.8
5.83	15.3	0.0339	6.80	16.4
5.05	15.3	0.0339	16.4	25.2
6.07	15.3	0.0339	57.0	35.2
5.67	15.3	0.284	0.706	17.7
6.78	15.3	0.284	2.21	25.5
6.75	15.3	0.284	9.75	38.0

The nonzero intercepts of the lines for the Cr^{2+} dependence in Figure 1 are evidence for a contribution to the reaction rate from the spontaneous aquation of I which is independent of the $[Cr^{2+}]$. The variation of the value of the intercept of the lines in Figure 1 depending upon the $[H^+]$ indicates that the spontaneous aquation of I has an inverse acid dependence. Furthermore, a plot of the intercepts in Figure 1 *vs.* $[H^+]^{-1}$ is linear with a nonzero intercept; therefore, the spontaneous

Table III. Rate Data for the Cr^{2+}-Catalyzed Aquation of Pentaaquochromium(III) Complexes[a]

Ligand	k_2, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Ref
	5×10^{-5} [b]			c
$-O_2CCH_3$	2.5×10^{-5}	22	−5	d
	4.7×10^{-4}	18[f]	−13[f]	This work
H_2O	1.2×10^{-4}	22		e
	1.3×10^{-3}	19	−8	g

[a] All rates at 25° and $\mu = 1.0$ except where indicated. [b] $\mu = 0.10$. [c] Preliminary results of work now in progress. [d] Reference 10. [e] A. Anderson and N. A. Bonner, *J. Amer. Chem. Soc.*, 76, 3826 (1954). [f] $\mu = 0.40$. [g] Reference 9.

aquation of I involves two pathways, one independent of the acid concentration, k_0, and the other inverse in acid, k_1. In Figure 2 the nonzero intercepts of the acid-dependence lines at fixed $[Cr^{2+}]$ are the same within the experimental error and correspond to k_0.

Figures 1 and 2 indicate a pathway for the aquation of I which is first-order in $[Cr^{2+}]$ and inverse in $[H^+]$. In Figure 1 the lines conform to the equation

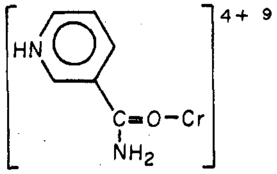
$$k_{obsd} = k_0 + \frac{k_1}{[H^+]} + \frac{k_2[Cr^{2+}]}{[H^+]} \tag{3}$$

The intercept of the lines equals $(k_0 + k_1/[H^+])$ and the slope of the lines equals $k_2/[H^+]$. In Figure 2 the lines also conform to eq 3 with the intercept of the lines equaling k_0 and the slope of the lines equaling $(k_1 + k_2[Cr^{2+}])$. From the above data the calculated values of the rate constants at $\mu = 1.0$ and 25° are $k_0 = (3.07 \pm 0.18) \times 10^{-6}$ sec^{-1} (from the intercept in Figure 2), $k_1 = (2.77 \pm 0.29) \times 10^{-7}$ M sec^{-1} (from the slope in Figure 2), $k_1 = (2.83 \pm 0.18) \times 10^{-7}$ M sec^{-1} (from the intercepts in Figure 1), and $k_2 = (4.74 \pm 0.05) \times 10^{-4}$ sec^{-1} (from the slope in Figure 1).

It should be noted that our data do not rule out a $k_3 \cdot [Cr^{2+}][I]$ pathway. However the agreement of the intercept values in Figure 2 and the agreement of the values of k_1 calculated by two different means allow an upper limit of 10^{-5} M^{-1} sec^{-1} to be placed on the value of k_3. An independent measure of k_0 would help elucidate the presence of the k_3 pathway, but it is negated by the appreciable oxidation of I and isonicotinamidepentaammineruthenium(II) at $[Cr^{2+}] = 0.0$ by perchloric acid. Also the value of k_0 varies with the nature of the supporting electrolyte being 3.07×10^{-6} sec^{-1} in 1.0 M $LiClO_4$-$HClO_4$ and 1.02×10^{-5} sec^{-1} in 0.1 M LiBr-HBr.

At $\mu = 0.40$ the values of k_0, k_1, and k_2 are $(1.7 \pm 0.9) \times 10^{-6}$ sec^{-1}, $(2.72 \pm 0.50) \times 10^{-7}$ M sec^{-1}, and $(3.51 \pm 0.06) \times 10^{-4}$ sec^{-1}, respectively. From Eyring plots of the temperature-dependence data in Table II, $\Delta H^{\ddagger} = 18.1 \pm 0.4$ kcal mol^{-1} and $\Delta S^{\ddagger} = -13.1 \pm 0.3$ eu for the k_2 pathway.

The observed Cr^{2+}-catalyzed pathway, k_2, for the aquation of I most likely corresponds to an inner-sphere electron-transfer mechanism involving a hydroxide-bridged transition state ($Ru^{II}LCr^{III}OHCr^{II}$). A similar mechanism has been proposed for the Cr^{2+}-catalyzed aquation of $CrCl^{2+}$,[7] of CrI^{2+},[8] of and of $CrOAc^{2+}$.[10]



In Table III are summarized the kinetic results for the Cr^{2+}-catalyzed aquation of some pentaaquochromium(III) complexes with oxygen-donor ligands. For this pathway $k_2 = k_2'K_a$, where K_a is the acidity constant for the chromium(III) complex and k_2' is the true rate constant for the electron-transfer process. Nordmeyer and Taube[9] have explained the increased reactivity of the protonated nicotinamidechromium(III) ion compared to the acetato- and aquochromium(III) ions on the basis of the enhanced acidity of the protonated nicotinamidechromium(III) ion due to the lower basicity of nicotinamide resulting from the presence of the proton on the ligand. Also the charge effects of the protonated ligand should increase the ease of transfer of negative charge to chromium(III). Accordingly on the basis of the above arguments the (ruthenium(II) isonicotinamide)chromium(III) and (ruthenium(II) nicotinamide)-chromium(III) ions would be expected to be more reactive than the protonated nicotinamidechromium(III) ion.[11] The reverse reactivity is observed and can be explained on the basis of significant ruthenium-to-ligand charge transfer which would increase electron density on the heterocyclic ligand re-

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(11) Although the rate comparison is not direct in the ruthenium(II) isonicotinamide *vs.* protonated nicotinamide case, the preliminary results on the ruthenium(II) nicotinamide rate studies justify such a comparison. The difference in k_2 between ruthenium(II) isonicotinamide and ruthenium(II) nicotinamide is attributed primarily to ionic strength effects.

sulting in an increase in the basicity of the ruthenium(II)-ligand species and a decrease in the acidity of the chromium(III) ion compared to the protonated nicotinamidechromium(III) ion.

The intense visible absorption band characteristic of pentaammineruthenium(II) complexes with a heterocyclic ligand and the greater basicity of pyrazinepentaammineruthenium(II) compared to uncoordinated pyrazine have been accounted for on the basis of ruthenium-to-ligand charge transfer.[12] The present work offers further evidence for significant metal-to-ligand back-donation in ruthenium(II) complexes with heterocyclic ligands.

Acknowledgment. R. W. C. is grateful for a Non-Service Fellowship supported by the University of Tennessee.

Registry No. I, 50639-78-6; Cr^{2+}, 22541-79-3; (ruthenium(II) nicotinamide)chromium(III) ion, 50639-79-7.

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Cobaloxime Nitrosyl. Reaction with Molecular Oxygen and Formation of Coordinated Nitrato Complexes

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Reaction of coordinated nitrosyl with molecular oxygen has been observed to produce coordinated nitro groups.[1,2] Formation of coordinated nitrate is restricted to a few ruthenium complexes.[3,4] The most extensive study of the reaction of nitrosyl complexes with oxygen has been carried out by Clarkson and Basolo,[1] who studied principally complexes of the general type Co(L)NO, where L is a quadridentate dinegative Schiff base chelate or two bidentate dialkyldithiocarbamate ligands. These complexes react most readily in the presence of monodentate ligands, B, such as pyridine (py) and tri-*n*-butylphosphine (Bu_3P). From the determination of the dependence of the rate of reaction on [B], it was concluded that BCo(L)NO complexes were formed. The low formation constants prevented spectral characterization of BCo(L)NO. This complex most likely reacts with oxygen to form $BCo(L)NOO_2$, where NOO_2 is angular O-N-O-O coordinated through N.[1] This peroxy intermediate then reacts with another BCo(L)NO complex to produce $BCo(L)NO_2$ complexes.

During the course of an investigation of cobaloximes containing ligands with high trans effects, we had occasion to prepare cobaloxime nitrosyl $Co(DH)_2NO$ (where DH is the monoanion of dimethylglyoxime). The general interest in the activation of small molecules by transition metals and recent interest in the oxidation of nitrosyls led us to investigate the reaction of cobaloxime nitrosyl with oxygen. It has been previously reported that in the absence of added ligands, B, the nitro complex $(H_2O)Co(DH)_2NO_2$ is formed.[2]

We have found that the major product of the oxidation of $BCo(DH)_2NO$ in CH_2Cl_2 is usually the O-bonded nitrato compound, $BCo(DH)_2NO_3$, found in amounts greater than 50% when B = *t*-Bu(py), CNpy, Me(IMD), and $P(C_6H_5)_3$.[5] The second major product is the expected nitro compound formed in amounts less than 50%. The reaction was not clean in that small amounts of side products which could not be identified were also formed (<10%). After discovery of this reaction, we began preliminary studies to determine the mechanism. However, the product distribution, while being little dependent on a variety of factors such as the nature and concentration of B, the solvent, and the total complex concentration, was not exactly reproducible. The product ratio of nitrato to nitro also did not change significantly on addition of a variety of cobalt(II) catalysts[6,7] or of chelating agents such as bipyridine. In every case (over 50 reactions) the nitrato product was formed and in amounts greater than the nitro product.

The ratio of products was also independent of added nitrate or nitro products after subtraction of the contribution of product initially added. In this connection, we observed that the nitrato complex does not react with the nitrosyl complex in the presence of added B.

Because of the above difficulties and the rapidity of the reaction (complete in *ca.* 15 sec), we have not been able to determine the reaction mechanism. However, the formation of nitrato complexes from oxidation of nitrosyl compounds has only been observed for ruthenium complexes. These may react through dioxygen complex intermediates.[3,4] We report here our observations substantiating nitrate formation for one ligand, *t*-Bu(py), and one solvent, CH_2Cl_2. We also report several observations on the spectral properties of cobaloxime nitrosyl.

Results

A methylene chloride solution (*ca.* 0.01 *M*) of $Co(DH)_2NO$[2] under nitrogen exhibits a pmr signal at τ 7.58 assignable to the four equivalent bis(dimethylglyoximato) methyl groups. Addition of base, B, causes an upfield shift of the signal. The chemical shift depends on B in a manner consistent with eq 1. The observation of only one bis(dimethylglyoximato) methyl resonance for the nitrosyl complexes when [complex]/[B] > 1 and the variation in chemical shift of the ligand resonances (such as the *t*-Bu groups in *t*-Bu(py)) are consistent with eq 1 being rapid on the pmr time scale. For example, only an average *t*-Bu resonance is observed for coordinated and free *t*-Bu(py) (when [complex] > [*t*-Bu(py)], the *t*-Bu resonance occurs at τ 8.79 and shifts to a limiting low-field value of τ 8.68 when [complex] << [*t*-Bu(py)]).

$$Co(DH)_2NO + B \rightleftharpoons BCo(DH)_2NO \qquad (1)$$

In the presence of excess *t*-Bu(py), the bis(dimethyl-

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(5) Abbreviations used are *t*-Bu(py) = 4-*tert*-butylpyridine, CNpy = 4-cyanopyridine, and Me(IMD) = 1-methylimidazole. Chemical shifts observed for the methyloxime resonances for nitrato and nitro, respectively, are as follows: CNpy, τ 7.62 and 7.72; Me(IMD), τ 7.60 and 7.72; $(C_6H_5)_3P$, τ 7.95 and 8.04. The last compound has been reported previously. The high-field positions of the $(C_6H_5)_3P$ compounds are the result of anisotropic shielding of the phenyl groups and the resonances are split by phosphorus, J = 0.7 Hz (NO_3) and 1.5 Hz (NO_2).

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