$$k_{\text{obsd}} = \frac{k_{-1}k_2[\text{Mpz}^+] + k_1k_{-2}[\text{L}]}{k_1[\text{L}] + k_2[\text{Mpz}^+]} \qquad (2)$$

At high Mpz^+(aq) concentration k_{obsd} reduces to k_{-1}, the specific rate of loss of the coordinated ligand L. In this region of rate saturation the observed rate constant should be independent of the nature of the incoming ligand. This was verified by experiments in which isonicotinamide was substituted for Mpz^+(aq) (black point in Figure 1).

The variation of k_{-1} with temperature for the two leaving ligands was studied in the 10–30° temperature range, and the results are presented in Table I. Variation of k_{-1} with $[\text{H}^+]$ in the narrow pH range employable in this study was neither expected nor encountered.

The dependence of k_{-1} on temperature for the two complexes was investigated in the 10–30° interval, and the results are presented in Table I. Calculated activation parameters for amine loss from the ion $\text{Fe(CN)}_5\text{NH}_3^{3-}$(aq) are $\Delta H^\ddagger = 22.2 \pm 1.3$ kcal/mol and $\Delta S^\ddagger = 8 \pm 4$ cal deg^{-1} mol^{-1} with $k_{-1} = (1.75 \pm 0.05) \times 10^{-2}$ sec^{-1} at 25°, pH 7.2, and $\mu = 1$ *M*. For the complex $\text{Fe(CN)}_5\text{NH}_2\text{CH}_3^{3-}$(aq), $\Delta H^\ddagger = 23.0 \pm 1.3$ kcal/mol and $\Delta S^\ddagger = 7 \pm 4$ cal deg^{-1} mol^{-1} with $k_{-1} = (2.8 \pm 0.1) \times 10^{-3}$ sec^{-1} at 25°, pH 8.6, and $\mu = 1$ *M*.

The results of a study of the kinetics of dissociation of pentacyanoiron(II) complexes of aromatic N heterocycles[1] are summarized in Table II. These are similar to the results of the experiments described in this work in that analogous rate laws were observed in the two studies. Also, in both cases moderately positive entropies of activation were calculated for the k_{-1} step, implying a common dissociative-type mechanism.

However, other aspects of the two sets of results are dissimilar. The specific rates of dissociation of the saturated amine complexes are 2–40-fold greater than those of the unsaturated class. Also, the k_{-1} values found for the saturated ligands correlate inversely with the ligand basicities, whereas for the unsaturated leaving groups, k_{-1} increases slightly with increasing ligand basicity.

If the steric factors affecting k_{-1} are considered constant for the pentacyanoiron(II) complexes treated herein, the following estimate can be made of back-bonding stabilization energies in the complexes of aromatic N heterocycles. Given that the rate of ligand loss for the two saturated amine complexes correlates inversely with ligand basicity, we propose that the rate of dissociation of a particular nitrogen base should be related to its $\text{p}K_{\text{HL}}$ value by an equation of the form $\log k_{-1} = A + B(\text{p}K_{\text{HL}})$.[7] Using appropriate values of k_{-1} and the $\text{p}K_{\text{HL}}$ values of the ammonium and methylammonium ions, one can calculate values of k_{-1} based on the $\text{p}K_{\text{HL}}$ values of the ligands in Table II. For 4-methylpyridine, pyridine, isonicotinamide, and pyrazine, the calculated k_{-1} values exceed the measured ones by factors of 10^3, 3×10^3, 4×10^4, and 4×10^6, respectively. The rate factors may be converted, employing transition-state theory,[8] into enthalpy factors, 4.1, 4.7, 6.3, and 8.9 kcal/mol, respectively.

These values are the enthalpies of activation required for dissociation of the Fe(CN)_5^{3-} complexes of certain unsaturated N heterocycles after accounting for the effect of the relative ligand basicities. The values can be considered as approximate upper limits to the back-bonding energies. Because they probably include effects other than π bonding,[9] the enthalpies may be significantly greater than the true back-bonding stabilization energies.

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Registry No. $\text{Fe(CN)}_5\text{NH}_3^{3-}$, 13717-31-2; $\text{Fe(CN)}_5\text{CH}_3\text{NH}_2^{3-}$, 20774-55-4.

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Phosphorus-31 Nuclear Magnetic Resonance Spectra of Catalytically Active Nitrosyl Complexes

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Numerous workers have shown recently that transition metal–nitrosyl complexes may function as hydrogenation catalysts.[1-5] Catalysis by coordinatively saturated species is unusual. One interpretation[1] suggests that phosphine dissociation occurs (eq 1). Osmometric molecular weights of

$$\text{M(NO)L}_n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{M(NO)L}_{n-1} + \text{L} \qquad (1)$$

300 and 800 were determined for $\text{RhNO(PPh}_3)_3$ and $\text{IrNO(PPh}_3)_3$ (formula weights 920 and 1009, respectively).[6] The second suggestion[2] for the efficacy of metal nitrosyls as catalysts involves an intramolecular redox process $\text{M}^q(\text{NO}^+) \rightarrow \text{M}^{q+2}(\text{NO}^-)$, with simultaneous decrease in the MNO bond angle from 180 to 120–140°.

We present here the results of a ^{31}P nmr study of $\text{MNO(PPh}_3)_3$ (M = Co, Rh) and $\text{Rh(NO)Cl}_2(\text{PPh}_3)_2$. Phosphine exchange in $\text{RhNO(PPh}_3)_3$ is shown to occur *via* a dissociative pathway.

Experimental Section

Materials. $\text{CoNO(PPh}_3)_3$[7] and $\text{RhNOCl}_2(\text{PPh}_3)_2$[8] were prepared by literature methods. $\text{RhNO(PPh}_3)_3$ was prepared by two routes.[2,8] Tetrahydrofuran (THF) was distilled from Na-K alloy. Nmr samples were prepared by degassing separately the solids and solvents (three

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Table I. Line Width Data and Kinetic Parameters for $RhNO(PPh_3)_3$ at 30°

$[RhNO(PPh_3)_3]$, *M*	$[PPh_3]$, *M*	$\Delta\nu_{RhNO(PPh_3)_3}{}^a$	$\Delta\nu_{PPh_3}{}^a$	$3\tau_{RhNO(PPh_3)_3}{}^{-1}$	$\tau_{PPh_3}{}^{-1}[PPh_3]/[RhNO(PPh_3)_3]$
0.198	0.497	3.6	5.1	34	40
0.113	0.530	4.3	3.0	41	44
0.037	0.518	4.0	0.9	38	39
5.02×10^{-3}	0	4.2		40	
0.108[b]	0.609	3.3	1.5	31	27

[a] Exchange contribution to line width, in Hz. [b] In C_6H_6.

freeze–thaw cycles) and distilling the latter directly into the loaded nmr tube. Sample tubes were then sealed off under vacuum.

Spectra. ^{31}P nmr spectra were recorded in 5-mm (o.d.) tubes using the Fourier transform technique at both 24.3 and 40.5 MHz, the latter employing a Varian XL-100 spectrometer. All spectra employed white-noise proton decoupling. Pulse delay times at room temperature were typically 6 sec, but increased relaxation rates at low temperatures in some solvents allowed pulse delay to be reduced to 0.7 sec with no decrease in spectral quality. This observation has been made before[9] and represents a useful technique for speeding data collection. Chemical shifts are with respect to external 85% H_3PO_4, downfield shifts being negative. Triphenylphosphine oxide served as an internal line width standard. Separate experiments showed this compound does not interact with $RhNO(PPh_3)_3$. The full width at half-height ($\Delta\nu^0{}_{1/2}$) was typically 0.9 Hz for the phosphine oxide. Lifetimes and line widths are related by the equation $\tau^{-1} = \pi(\Delta\nu_{1/2} - \Delta\nu^0{}_{1/2})$, line widths being read directly from the digitized spectra.

Results

The ^{31}P nmr spectrum of $RhNO(PPh_3)_3$ in THF at 30° consists of a doublet centered about −48.8 ppm ($^1J_{Rh-P}$ = 175 Hz). With $S/N = 300$ (4000 scans, Figure 1), no resonance is detectable at the chemical shift of free triphenylphosphine. This yields an upper limit for $k_1/k_{-1} = K$ in eq 1 of 2×10^{-4}. Phosphine exchange in $RhNO(PPh_3)_3$ was also investigated. The spectrum of 0.2 *M* $RhNO(PPh_3)_3$ in the presence of added PPh_3 (0.06 *M*), Figure 1, is not a simple superposition of the component spectra. Although $RhNO(PPh_3)_3$ remains a doublet at −48.8 ppm and PPh_3 appears at the chemical shift of free PPh_3, the latter signal is broad. This exchange broadening was investigated over a range of concentrations, and the results are summarized in Table I. To test for any solvent dependence of the exchange mechanism, the spectrum of a benzene solution containing $RhNO(PPh_3)_3$ and added PPh_3 was recorded. This result also appears in Table I. In a further attempt to detect free phosphine, the ^{31}P spectrum of a dilute (5×10^{-3} *M*) solution of $RhNO(PPh_3)_3$ in THF was recorded. Again, free triphenylphosphine was not observed. This result is consistent with the upper limit on *K* (eq 1) quoted above.

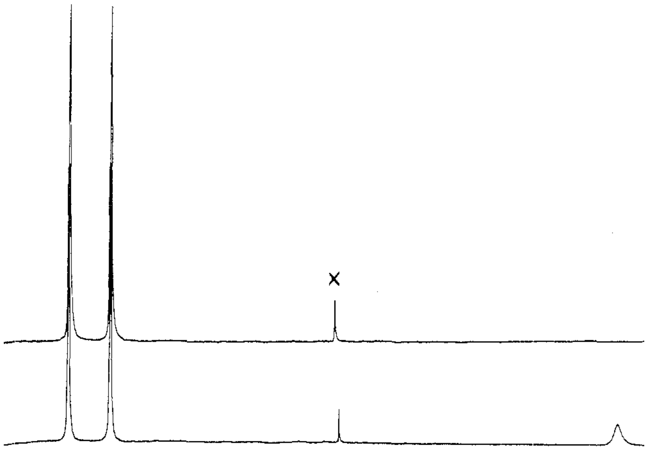

Figure 1. ^{31}P spectra of (upper) 0.2 *M* $RhNO(PPh_3)_3$ and (lower) 0.2 *M* $RhNO(PPh_3)_3$ with added PPh_3 (0.06 *M*) (X indicates $OPPh_3$). PPh_3 appears at lower right as a broad peak (5.6 ppm).

The ^{31}P spectrum of $CoNO(PPh_3)_3$ on C_6D_6 at room temperature (5000 scans) consists of an extremely broad resonance (full width at half-height 150 Hz) at approximately −58 ppm. This line width dilutes the signal to such an extent that ^{31}P nmr is nearly useless. Intermediate relaxation rates of quadrupolar nuclei (^{59}Co, $I = 7/2$) can broaden resonances of nuclei coupled to the quadrupolar nucleus.[10] The ^{31}P spectrum of $CoNO(PPh_3)_3$ at −55° in THF, which forms a glass at −65°, is a single line centered at −59.2 ppm with half-width of only 21 Hz. The sharpening of the line can be attributed to viscosity effects; high viscosity effectively decouples quadrupolar nuclei from other spins. Since low temperatures increase viscosity, this phenomenon has been termed "thermal decoupling" and has been reported previously for ^{14}N, ^{11}B, and ^{51}V.[10] The technique is likely to be effective for improving *S/N* of nuclei strongly coupled to ^{59}Co in symmetric molecules. The low-temperature ^{31}P spectrum of $CoNO(PPh_3)_3$ shows no resonance at the chemical shift of free phosphine.

The ^{31}P nmr spectrum of $Rh(NO)Cl_2(PPh_3)_2$ at room temperature in CH_2Cl_2 consists of a doublet ($^1J_{Rh-P}$ = 104 Hz) centered about −24.8 ppm. Here again there is no evidence for free phosphine. The single phosphorus chemical shift is consistent with a square-pyramidal structure with phosphines trans, as has been found[11] for $Ir(NO)Cl_2(PPh_3)_2$.

$Rh(NO)Cl_2(PPh_3)_2$ is coordinatively unsaturated if the RhNO moiety is bent. To test for exchange of coordinated phosphine with added free phosphine, the ^{31}P spectrum of a saturated (10^{-3} *M*) CH_2Cl_2 solution of this complex with 2×10^{-3} *M* added PPh_3 was recorded. This spectrum is a superposition of the spectra of the components, implying that exchange, if it occurs at all, is slow at these concentrations.[12]

Discussion

The ^{31}P nmr spectra reported here indicate chemical equivalence of the three phosphines in $MNO(PPh_3)_3$, M = Co, Rh, consistent with the pseudotetrahedral structures determined for $IrNO(PPh_3)_3$[13a] and $RhNO(PF_3)_3$.[13b] The ^{31}P nmr spectra show no dissociated phosphine for the catalytically active species $RhNO(PPh_3)_3$ and $Rh(NO)Cl_2(PPh_3)_2$. Thus, the very low molecular weight determined for $RhNO(PPh_3)_3$ is suspect. There is a well-established history of erroneous

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[12] Because of the very low concentrations involved, it is more precise to say only that the lifetime of coordinated or free phosphine exceeds $(\pi\Delta\nu_{1/2})^{-1} \approx 0.1$ sec.

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osmometric molecular weights for low-valent metal complexes as a result of reaction with oxygen.[14,15] $CoNO(PPh_3)_3$ also shows a single resonance with no evidence for phosphine dissociation. Since sterically demanding phosphines like PPh_3 maximize ligand dissociation,[16] eq 1 will lie farther to the left for analogous nitrosyl complexes containing mixed (alkyl)(aryl)phosphines. Phosphine dissociation thus occurs at most to a limited extent.

At 30°, exchange of phosphine coordinated to $RhNO(PPh_3)_3$ with free PPh_3 is detectable as line broadening of the free PPh_3 resonance. If an intramolecular redox process is energetically accessible, exchange might well occur *via* an associative mechanism. Substitution reactions of nitrosyl complexes frequently exhibit S_N2 kinetics.[17] For the exchange studied here, an associative mechanism predicts $\tau_L^{-1} \propto [RhNOL_3]$ and $\tau_{RhNOL_3}^{-1} \propto [L]$ where $L = PPh_3$. In fact, the phosphorus line width in $RhNO(PPh_3)_3$ is the same in all spectra recorded, including those without added phosphine. This line width is significantly greater than that of an internal standard, however.

Phosphine exchange by a dissociative pathway is shown in eq 1. For this equilibrium, the following relationships are valid

$$\tau_L^{-1} = k_1[RhNOL_3][L]^{-1} \qquad (2)$$

$$\tau_{RhNOL_3}^{-1} = k_1/3 \qquad (3)$$

Here τ_{RhNOL_3} represents the average lifetime of a complexed phosphine, which is the quantity measured experimentally. This mechanism correctly predicts the most obvious characteristic of the data in Table I: the line widths of the $RhNOL_3$ resonances are concentration independent. Values of k_1 derived from the line width of free triphenylphosphine (Table I) agree with those derived from eq 3. Since tetrahydrofuran is potentially a coordinating solvent, rate data were also obtained on a benzene solution of $RhNO(PPh_3)_3$ and PPh_3. The value of k_1 does not differ significantly from that in THF, suggesting that $RhNO(PPh_3)_2$ is a coordinatively unsaturated species and not the solvent (S) adduct $RhNO(PPh_3)_2S$.

Phosphine exchange of coordinatively saturated phosphine-metal-carbonyl complexes typically proceeds by a dissociative path. In contrast, the coordinatively unsaturated complexes MX_2L_2 (M = Fe, Co, Ni) all exchange phosphine by an associative pathway;[18] five-coordinative MX_2L_3 complexes are actually isolable in some instances. The mechanism of exchange of free phosphine with $RhNO(PPh_3)_3$ thus provides no evidence for NO functioning as an electron sink. However, this cannot be taken as evidence that linear-bent nitrosyl tautomerism is not catalytically significant. Steric factors are almost certainly important in this system. They may actually dominate the kinetics, since the bulkiness of triphenylphosphine promotes dissociation. Among six-coordinate complexes, a *fac*-$MX_3(PPh_3)_3$ complex, which bears an obvious structural similarity to $RhNO(PPh_3)_3$, has never been structurally characterized. An associative mechanism for phosphine exchange is probably sterically inaccessible to $RhNO(PPh_3)_3$. Excluding sterically atypical hydride complexes, there are no structurally characterized complexes with four triphenylphosphine ligands.[19] Solids of formula $M(PPh_3)_4$ may actually have one phosphine trapped in the lattice. Finally, steric effects have been shown to alter the mechanism of exchange of main group acid-base complexes.[20]

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Registry No. $CoNO(PPh_3)_3$, 18712-92-0; $RhNO(PPh_3)_3$, 51349-76-9; $Rh(NO)Cl_2(PPh_3)_2$, 40231-80-9; ^{31}P, 7723-14-0.

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Barium Pernitride from Thermal Decomposition of Barium Azide

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Various substances described as alkaline earth pernitrides have been reported.[1] All are black, reactive materials which yield X-ray diffraction patterns typical of amorphous compounds. The strontium pernitride prepared by vacuum pyrolysis of strontium amide proved to have a small magnetic moment which increased with rising temperature.[2] The most easily prepared and most thoroughly studied higher nitrides are those resulting from the decomposition of barium, strontium, and calcium azides under hydrocarbons.[1e] Of these, the barium compound is most nearly stoichiometric, being approximately Ba_3N_4. Attempts by Linke and coworkers[3] further to characterize these pernitrides by infrared, Raman, and mass spectrometry resulted in few revealing results. They showed that considerable hydrazine is formed during slow hydrolysis of the pernitrides and conjectured that the nitrogen atoms in pernitrides exist in some sort of polymeric chain or net structure. Barium pernitride has been employed to effect aldol and ester condensations and to prepare anhydrous hydrazine and alkaline earth hydrazides.[4] It converts dimethyl sulfoxide to an amorphous polymeric substance.[5]

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