Inorg. Chem. **1993,** *32,* 4214–4217

Photoprotonation of a Metal Nitride Complex

William J. Vining[†]

Department of Chemistry, Hartwick College, Oneonta, New York 13820

Gregory A. Neyhart, Stephan Nielsen,[‡] **and B. Patrick Sullivan**[*]

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838

Received February 11, 1993

Protonation of both the ground and the excited states of *trans*-$NRe(R_2PCH_2CH_2PR_2)_2Cl^+$ has been shown to occur in HCl solution (R = Me). The product is the imido complex *trans*-$HNRe(R_2PCH_2CH_2PR_2)_2Cl^{2+}$. Titration of the ground and excited states yields apparent p*K* values of ca. −1.0 and 4.5, respectively, demonstrating a profound increase in bascisity in the excited state. This change, which can be rationalized by a simple orbital diagram, is due to an increase in electron density at the nitride nitrogen in the excited state. The related complex *trans*-$NRe(CN)_4(H_2O)^{2-}$ exhibits an apparent excited-state p*K* value of 3.6, indicating that "tuning" of the excited-state properties is possible by large changes in coordination sphere composition.

Reactions of complexes containing transition metal–main group multiple bonds are of importance in areas as diverse as biology[1a,b] and industrial chemistry.[1a] Although the ground-state chemistry of metal–element multiple bonds, specifically those involving alkylidyne,[2] oxo,[3] imido,[4] and nitrido[5] groups, has expanded rapidly in recent years, that of the excited state has not. Systematic studies of their photochemistry and photophysics are rare although it is reasonable to assume that a characteristic core of photochemical reactions should exist. Of great interest in this regard is chemistry that could result from enhanced electrophilicity or nucleophilicity of the excited state, for example, atom transfer, photocycloaddition, or photometathesis. In several key studies, photochemistry inherent to the excited states of multiply-bonded complexes has been identified. These include W alkylidynes that exhibit photoredox or atom-transfer reactions[2] and an Os nitride that undergoes photoredox coupled to subsequent reaction at the nitride fragment.[5g]

Excited-state acid–base reactions of inorganic compounds are poorly understood compared to those of their organic counterparts. The principal studies in this area have concentrated on metal complexes of polypyridine or polypyridine-like ligands where metal-to-ligand charge transfer (MLCT) radically changes the charge distribution from that of the ground state. An early example is that of $Ru(DCbpy)_3^{2+}$ (DCbpy = 4,4′-dicarboxy-2,2′-bipyridine), which upon MLCT excitation becomes a poorer acid.[6] On the other hand, the $Ru(bpz)_3^{2+}$ (bpz = 2,2′-bipyrazine) MLCT excited state is a stronger base than the ground state.[7] The behavior of both can be rationalized by an increase in negative charge on the polypyridine ligand in the excited state. In the interesting case of *cis*-$Ru(bpy)_2(CN)_2$, the ancillary cyano ligands become weaker bases because of the formation of an electron-deficient "Ru(III)" core in the excited state to which the cyano ligands are bound.[8] Several other MLCT excited-state states that exhibit enhanced acidity or basicity have been studied and are summarized nicely by Kalyanasundaram in a contemporary monograph.[9]

Recently it has become apparent from spectroscopic and reactivity data that the excited states of complexes containing metal–element multiple bonds can possess acid–base properties very different from those of their ground states, in both a kinetic and a thermodynamic sense.[3c] Here we report the first example of increased basicity of a nitrido complex in its thermally equilibrated excited state and compare this to the ground-state basicity. Our work has concentrated on the excited-state properties of the recently prepared complexes *trans*-$NRe(R_2PCH_2CH_2PR_2)_2X^+$ (R = Me, X = Cl, Br; R = Et, X = Cl), which are rare examples of nitrido complexes exhibiting fluid solution luminescence at room temperature.[4,5a] The emission

---

[*] Author to whom correspondence should be addressed.

[†] NSF Research Opportunity Award recipient.

[‡] 1991 summer student from the Royal Institute of Technology, Stockholm, Sweden.

(1) (a) Mayer, J.; Nugent, W. A. *Metal-Ligand Multiple Bonds*; Academic Press: New York, 1988. (b) Dehnicke, K.; Strahle, J. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 955.

(2) (a) Vogler, A.; Kisslinger, J.; Roper, W. R., *Z. Naturforsch.* **1983**, *38B*, 1506. (b) Mayr, M. A.; Kjeisberg, K. S.; Lee, M. F.; Asaro, Hsieh, T.-C. *Organometallics* **1987**, *6*, 2610. (c) Sheridan, J. B.; Paurreau, D. B.; Geoffroy, G. L. *Organometallics* **1988**, *7*, 289. (d) Brower, D. C.; Stoll, M.; Templeton, J. L. *Organometallics* **1989**, *8*, 2792. (e) Kingsbury, K. B.; Carter, J. D.; McElwee-White, L. *J. Chem. Soc., Chem. Commun.* **1990**, 624. (f) Green, M. *J. Organomet. Chem.* **1986**, *300*, 93. (g) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, G. A. *J. Chem. Soc., Chem. Commun.* **1985**, 68. (h) Carter, J. D.; Kingsbury, K. B.; Wilde, A.; Schoch, T. K.; Leep, C. J.; Pham, E. K. *J. Am. Chem. Soc.* **1991**, *113*, 2947. (i) Bocarsly, A. B.; Cameron, R. E.; Rubin, H.-D.; McDermott, G. A.; Wolff, C. R.; Mayr, A. *Inorg. Chem.* **1985**, *24*, 3978.

(3) (a) Winkler, J. R.; Gray, H. B. *Inorg. Chem.* **1985**, *24*, 346. (b) Thorp, H. H.; Van Houten, J.; Gray, H. B. *Inorg. Chem.* **1989**, *28*, 889. (c) Liu, W.; Welch, T. W.; Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 4044. (d) Che, C.-M.; Yam, V. W.-W.; Gray, H. B. *J. Chem. Soc., Chem. Commun.* **1987**, 948. (e) Che, C.-M.; Cheng, W. K. *J. Am. Chem. Soc.* **1986**, *108*, 4644. (f) Yam, V. W.-W.; Che, C.-M.; Tang, W. T. *J. Chem. Soc., Chem. Commun.* **1988**, 100.

(4) Neyhart, G. A.; Bakir, M.; Boaz, J.; Vining, W. J.; Sullivan, B. P. *Coord. Chem. Rev.* **1991**, *111*, 27.

(5) (a) Neyhart, G. A.; Seward, K. J.; Boaz, J.; Sullivan, B. P. *Inorg. Chem.* **1991**, *30*, 4486. (b) Pollagi, T. P.; Stoner, T. C.; Dallinger, R. F.; Gilbert, T. M.; Hopkins, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 704. (c) Hopkins, M. D.; Miskowski, V. M.; Gray, H. B. *J. Am. Chem. Soc.* **1986**, *108*, 6908. (d) Cowman, C. D.; Trogler, W. C.; Mann, K. R.; Poon, C. K.; Gray, H. B. *Inorg. Chem.* **1976**, *15*, 1747. (e) Che, C.-M.; Lau, T.-C.; Lam, H.-W.; Poon, C.-K. *J. Chem. Soc., Chem. Commun.* **1989**, 114. (f) Che, C.-M.; Lam, H.-W.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1989**, 1529. (g) Lam, H.-W.; Che, C.-M.; Wong, K.-Y. *J. Chem. Soc., Dalton Trans.* **1992**, 1411.

(6) (a) Giordano, P. J.; Bock, C. R.; Wrighton, M. S.; Interrante, L. V.; Williams, R. F. X. *J. Am. Chem. Soc.* **1977**, *99*, 3187. (b) Ferguson, J.; Mau, A. W. H.; Sasse, W. H. F. *Chem. Phys. Lett.* **1979**, *68*, 21. (c) Lay, P. A.; Sasse, W. H. F. *Inorg. Chem.* **1984**, *23*, 4142. (d) Shimidzu, T.; Iyoda, T.; Izaki, K. *J. Phys. Chem.* **1985**, *89*, 642.

(7) Crutchley, R. J.; Kress, N.; Lever, A. B. P. *J. Am. Chem. Soc.* **1983**, *105*, 1170.

(8) (a) Peterson, S. H.; Demas, J. N. *J. Am. Chem. Soc.* **1976**, *98*, 7880; **1979**, *101*, 6571. (b) Davila, J.; Bignozzi, C. A.; Scandola, F. *J. Phys. Chem.* **1989**, *93*, 1373.

(9) Kalyanasundaram K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: New York, 1992.

0020-1669/93/1332-4214$04.00/0

spectral properties provide a means to observe the excited-state protonation shown in eqs 1 and 2 by emission quenching. Equation 2 is a unique example of the photochemical formation of a metal imide from a metal nitride complex.

$$\mathrm{NRe(R_2PCH_2CH_2PR_2)_2Cl^+} \xrightarrow{h\nu} \mathrm{NRe(R_2PCH_2CH_2PR_2)_2Cl^{+,*}} \tag{1}$$

$$\mathrm{NRe(R_2PCH_2CH_2PR_2)_2Cl^{+,*}} + \mathrm{H^+} \rightleftharpoons \mathrm{HNRe(R_2PCH_2CH_2PR_2)_2Cl^{2+}} \tag{2}$$

Experimental Section

Materials. Solvents were from the Burdick and Jackson Co. and were purchased from the Aldrich Chemical Co. $[\mathrm{Me_3O}]\mathrm{PF_6}$ was also purchased from Aldrich Chemical Co. and was used as received. Phosphine reagents were purchased from the Strem Chemical Co. and were used as received. $\mathrm{NRe(PPh_3)_2Cl_2}$ was prepared as described recently,[10] which is a modification of a literature procedure.[11] $\mathrm{K_3[NRe(CN)_5]}$ and $\mathrm{K_2[NRe(CN)_4(H_2O)]}$ were prepared by the method of Johnson.[12]

Measurements. Ultraviolet and visible spectra were recorded using an HP 8452A diode array spectrophotometer. Samples were contained in 1.00-cm quartz cuvettes and were referenced to a solvent blank. Molar extinction coefficients were obtained from samples with absorbances between 0.1 and 1. Infrared spectra were recorded on a Midac FTIR either in $\mathrm{CH_2Cl_2}$ solution or in a KBr pellet.

Emission spectra were recorded using a SLM 8000C spectrofluorometer. Corrections for the variation of instrument response with wavelength were made with the use of programs supplied by the manufacturer.

^{1}H and ^{31}P NMR spectral data were collected using JEOL 270- and 400-MHz NMR spectrometers with $\mathrm{CD_3CN}$ as solvent. Spectra were referenced either to the excess protio peaks in the solvent or to 85% $\mathrm{H_3PO_4}$.

Preparations. All reactions were conducted under a blanket of nitrogen. The products were stable to the atmosphere so that purification was done in air.

Preparation of $[\mathrm{NRe(Me_2PCH_2CH_2PMe_2)_2Cl}]\mathrm{Cl}$. An 800-mg sample of $\mathrm{NRe(PPh_3)_2Cl_2}$ (1.01 mmol) was added to 25 mL of ethanol in a 500-mL round-bottom flask in a nitrogen-filled glovebox. A 1.0-g amount of $\mathrm{Me_2PCH_2CH_2PMe_2}$ (5.88 mmol) was added to the flask, and the total volume was brought to 50 mL with ethanol. The flask was stoppered, removed from the glovebox, and rapidly transferred to a condenser containing a nitrogen flow with a minimum exposure to air. The mixture was heated to reflux under nitrogen with magnetic stirring. After 90 min, the insoluble, brick-colored starting material had disappeared leaving a yellow-orange solution. Reflux was maintained for another 60 min. The solution was cooled to room temperature, and the volume was reduced by rotary evaporation to about 5 mL. Precipitation was induced by the addition of 500 mL of diethyl ether. The ether mixture was stirred for 60 min, the ether was decanted, and the fluffy yellow solid was collected by suction filtration. The solid was washed with 3 × 25 mL of diethyl ether and dried by suction. The complex was purified by twice reprecipitating from a minimum amount of chloroform (ca. 25 mL, removing pale orange insoluble impurities by filtration) into diethyl ether (ca. 250 mL). This was followed by recrystallization from a 1:5 acetonitrile:toluene mixture under subdued light, with slow evaporation of the acetonitrile. Yield: 480 mg (85%). Metathesis of the hexafluorophosphate salt was achieved by dissolving the chloride salt in a ca. 0.05 M aqueous NaCl followed by the addition of excess $\mathrm{KPF_6}$. Recrystallization was again performed from a 1:5 acetonitrile:toluene mixture under subdued light, with slow evaporation of the acetonitrile. The solid so obtained was dried overnight *in vacuo*.

Characterization data for *trans*-$\mathrm{NRe(Me_2PCH_2CH_2PMe_2)_2Cl^+}$ are as follows. UV–visible spectrum in $\mathrm{CH_2Cl_2}$: $\lambda_{\mathrm{max}} = 238$ nm ($\epsilon = 4000$ $\mathrm{M^{-1}\,cm^{-1}}$), $\lambda_{\mathrm{sh}} = 257$ nm ($\epsilon = 2980$ $\mathrm{M^{-1}\,cm^{-1}}$), $\lambda_{\mathrm{max}} = 362$ nm ($\epsilon = 250$ $\mathrm{M^{-1}\,cm^{-1}}$). Infrared spectrum in $\mathrm{CH_2Cl_2}$: ν(Re–N) = 1059 $\mathrm{cm^{-1}}$. ^{1}H NMR spectrum in $\mathrm{CD_3CN}$ (ppm): δ 1.70 (12 H, s, br), 2.00 (12 H, s, br), 2.07 (8 H, t). ^{31}P NMR spectrum in $\mathrm{CD_3CN}$: 17.4 ppm vs $\mathrm{H_3PO_4}$. Anal. Calcd for $[\mathrm{NRe(Me_2PCH_2CH_2PMe_2)_2Cl}](\mathrm{PF_6})$: C, 21.16; H, 4.75; N, 2.06. Found: C, 22.13; H, 4.78; N, 1.68. The ^{1}H NMR spectrum of this sample revealed a small fraction of toluene present in the sample from recrystallization. Anal. Calcd for $[\mathrm{NRe(Me_2PCH_2CH_2PMe_2)_2Cl}](\mathrm{PF_6})\cdot 0.1\mathrm{C_7H_8}$: C, 22.10; H, 4.80; N, 2.03.

Preparation of $[\mathrm{MeNRe(Me_2PCH_2CH_2PMe_2)_2Cl}](\mathrm{PF_6})_2$. This reaction was performed inside a nitrogen-filled glovebox. To a 50-mL round-bottom flask containing 100 mg of $[\mathrm{NRe(Me_2PCH_2CH_2PMe_2)_2Cl}](\mathrm{PF_6})$ (9.15 mmol) was added 35 mL of $\mathrm{CH_2Cl_2}$ followed by 220 mg of $[\mathrm{Me_3O}]\mathrm{BF_4}$ (1.5 mmol). The flask was covered with aluminum foil, and the reaction mixture was then magnetically stirred for 2 h. At this point, the desired complex precipitated from solution presumably as a mixed salt. The flask was then removed from the glovebox, and the yellow-orange solid was collected by suction filtration. The complex was converted to the hexafluorophosphate salt by dissolution in a 2:1 mixture of 0.1 M HCl/MeOH (75 mL) followed by reprecipitation with 1 mL of a 6.1 M aqueous solution of $\mathrm{NH_4PF_6}$. The solid was collected by suction filtration and air-dried. Yield: 77 mg (62%).

Characterization data for [*trans*-$\mathrm{MeNRe(Me_2PCH_2CH_2PMe_2)_2Cl}$]$(\mathrm{PF_6})_2$ are as follows. UV–visible spectrum in $\mathrm{CH_3CN}$: $\lambda_{\mathrm{max}} = 296$ nm ($\epsilon = 2100$ $\mathrm{M^{-1}\,cm^{-1}}$), $\lambda_{\mathrm{sh}} = 412$ nm ($\epsilon = 150$ $\mathrm{M^{-1}\,cm^{-1}}$). The infrared spectrum in solid KBr showed the ν(Re–N) = 1059 $\mathrm{cm^{-1}}$ band present in the spectrum of the starting complex to be absent but two new bands to be present in this region at 922 $\mathrm{cm^{-1}}$ (w) and 1084 $\mathrm{cm^{-1}}$ (m). ^{1}H NMR spectrum in $\mathrm{CD_3CN}$ (ppm): δ 1.82 (6 H, m, br), 1.97 (6 H, m, br), 2.20–2.35 (11 H, m). ^{31}P NMR spectrum in $\mathrm{CD_3CN}$: 11.4 ppm vs $\mathrm{H_3PO_4}$. Anal. Calcd for $[\mathrm{MeNRe(Me_2PCH_2CH_2PMe_2)_2Cl}](\mathrm{PF_6})_2$: C, 18.57; H, 4.20; N, 1.66. Found: C, 18.60; H, 4.30; N, 1.72.

Procedure for Ground-State Protonation. The protonation behavior was studied by determination of the change in the absorption spectrum as a function of acid concentration. Solutions were prepared by diluting 1-mL aliquots of a stock solution (8.5×10^{-4} M [*trans*-$\mathrm{MeNRe(Me_2PCH_2CH_2PMe_2)_2Cl}$]$(\mathrm{PF_6})_2$ in 12 M HCl) to a volume of 4 mL using the appropriate amounts of 12 M HCl and distilled water. The final pH was measured by a Markson digital pH/mV meter.

Procedure for Excited-State Protonation. Excited-state protonation was demonstrated by the effects of pH on the emission intensity of the spectrum of *trans*-$\mathrm{MeNRe(Me_2PCH_2CH_2PMe_2)_2Cl^+}$. Solutions were prepared by diluting 1-mL aliquots of a stock solution (2.0×10^{-3} M [*trans*-$\mathrm{MeNRe(Me_2PCH_2CH_2PMe_2)_2Cl}$]Cl in aqueous solution) to a volume of 10 mL using the appropriate combinations of 0.1 M HCl, 0.1 M KOH, and 0.1 M KCl. The final pH was measured by a Markson digital pH/mV meter.

Results and Discussion

Ground-State Protonation of *trans*-$\mathrm{NRe(Me_2PCH_2CH_2PMe_2)_2Cl^+}$. Metal nitride complexes can be protonated to give the corresponding imides under a variety of acidic conditions depending on the nature of the central metal and the ancillary ligands. For example *trans*-$\mathrm{NMo^{IV}(Ph_2PCH_2CH_2PPh_2)_2F}$ is strong base (pK_a = 12.7; MeOH solution at 25 °C)[13] whereas the $\mathrm{Os^{VI}NH^{4+}}$ core is implied as an intermediate in the oxidation of $\mathrm{Os(NH_3)_6^{3+}}$ to $\mathrm{NOs(NH_3)_4(H_2O)^{3+}}$ in aqueous solution.[14] An analogous intermediate should be present in the reversible interconversion of $\mathrm{Os(NH_3)(trpy)Cl_2}$ and $\mathrm{NOs(trpy)Cl_2^{2+}}$ in aqueous solution.[15] Presumably, both of these intermediates are strong acids. Excited states based on metal nitride chromophores should possess acid–base properties radically different from those of their ground states and therefore could provide chemical pathways for novel chemistry.

Recently we described the preparation and excited-state properties of a series of complexes of the type *trans*-$\mathrm{NRe(R_2PCH_2CH_2PR_2)_2X^+}$ (R = Me, X = Cl, Br; R = Et, X = Cl) that possess the $\mathrm{Re^VN^{2+}}$ core.[5a] On further examination, we find that the prototypical complex *trans*-$\mathrm{NRe(Me_2PCH_2CH_2PMe_2)_2Cl^+}$ has feeble basicity in the ground state, being one-half protonated in HCl(aq) at a concentration of 9 M (pK_{app} ca. −1.0). This is illustrated in Figure 1 by its absorption spectral changes as a

---

(10) Sullivan, B. P.; Brewer, J. C.; Gray, H. B. *Inorg. Synth.* **1992**, *38*, 146.

(11) Chatt, J.; Falk, C. D.; Leigh, G. J.; Paske, R. J. *J. Chem. Soc. A* **1969**, 2288.

(12) Johnson, N. P. *J. Chem. Soc. A* **1969**, 1843.

(13) Henderson, R. A.; Davies, G.; Dilworth, J. R.; Thorneley, R. N. F. *J. Chem. Soc., Dalton Trans.* **1981**, 40.

(14) Buhr, J. D.; Winkler, J. R.; Taube, H. *Inorg. Chem.* **1980**, *19*, 2416.

(15) Pipes, D. W.; Bakir, M.; Vitols, S. E.; Hodgson, D. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 5507.

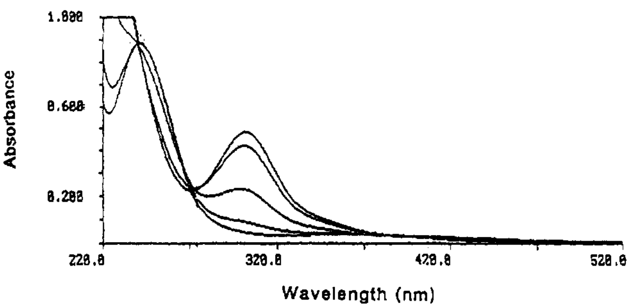


Figure 1. Change in the absorption spectrum of a 2.12 × 10^{-4} M [NRe(dmpe)$_2$Cl]Cl solution upon sequential addition of HCl. Proceeding from the lower absorbance at 309 nm, the concentrations of HCl are 3, 6, 9, 10, and 12 M, respectively.

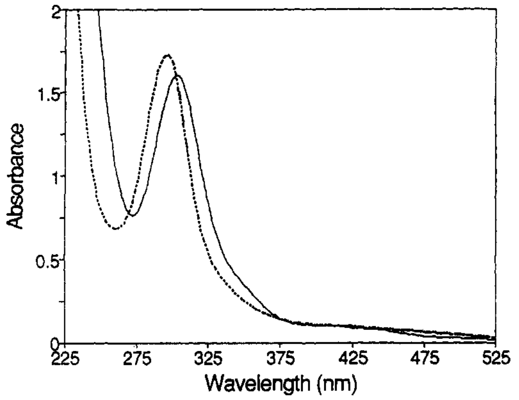


Figure 2. Comparison of the absorption spectra of HNRe(dmpe)$_2$Cl^{2+} (solid line; 2.0 × 10^{-4} M in 12 M HCl) and MeNRe(dmpe)$_2$Cl^{2+} (dashed line; 2.2 × 10^{-4} M in CH$_3$CN).

function of pH. Although isosbestic behavior is not well-maintained, the reaction can be demonstrated to be completely reversible upon addition of NaOH(aq).

That the limiting spectrum in Figure 1 corresponds to the formation of an imido complex (eq 3) is supported by comparison

$$\mathrm{NRe(R_2PCH_2CH_2PR_2)_2Cl^+ + H^+ \rightleftharpoons HNRe(R_2PCH_2CH_2PR_2)_2Cl^{2+}} \qquad (3)$$

of the electronic spectrum of presumed HNRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl^{2+} with that of the newly discovered methylimido complex MeNRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl^{2+} (Figure 2). The synthesis of this new complex was accomplished by reaction of NRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl$^+$ with the potent methylation agent [Me$_3$O]BF$_4$ in CH$_2$Cl$_2$ solution. Characterization was achieved using ^{31}P and ^{1}H NMR spectroscopies, elemental analysis, and UV–visible spectroscopy (see Experimental Section). Returning to Figure 2, it is seen that MeNRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl^{2+} and the protonated form of the nitride are indeed similar in the lower energy "d–d" region (λ_{max}(sh) = 412 nm, ϵ_{max} = 150, for the methylimido while λ_{max}(sh) = 408 nm, ϵ_{max} = 120, for the nitrido complex), which is assigned as $(d_{xy})^2 \rightarrow (d_{xy})^1(d_{xz}, d_{yz})^1$ in nature. In the LMCT (Cl → Re^V) region transitions occur at ca. 300–310 nm.[16]

Excited-State Protonation of NRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl$^+$. Figure 3 shows the emission spectrum of NRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl]$^+$ in aqueous 0.09 M KCl and in 0.09 M HCl. It is apparent that the emission intensity is substantially diminished in acid solution, but as indicated by the data shown in Figure 2, there is no protonation of the ground state at this pH. The purpose of KCl is to suppress the aquation equilibrium that occurs due to the strong kinetic trans effect of the ReN^{2+} core (eq 4) and to eliminate an ionic strength effect as a substantial factor in emission quenching. Although we have not evaluated the equilibrium constant for the reaction shown in eq 4, it is apparent

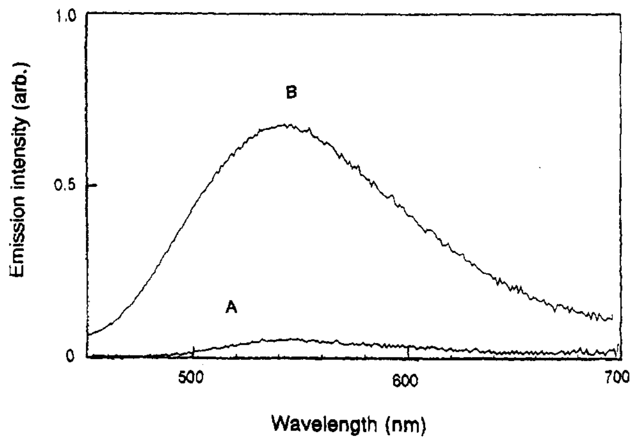


Figure 3. Emission spectrum of [NRe(dmpe)$_2$Cl]Cl (ca. 2 × 10^{-4} M) in (A) 0.09 M HCl and (B) 0.09 M KCl. Excitation wavelength is 360 nm.

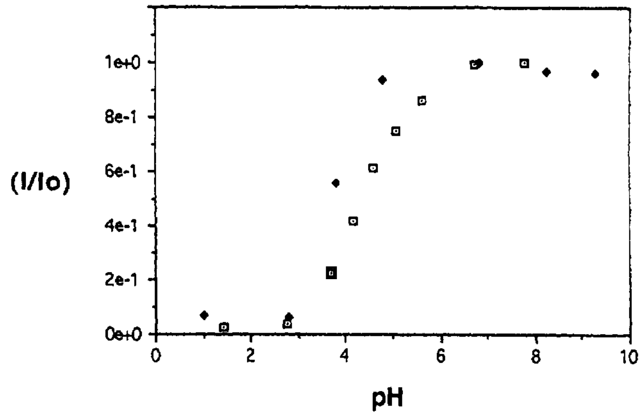


Figure 4. Titration curves for [NRe(dmpe)$_2$Cl]Cl (open squares) and K$_2$[*trans*-NRe(CN)$_4$H$_2$O] (solid diamonds). Shown are the plots of I/I_0 versus the pH of the solutions (I_0 is the intensity of emission in the absence of H$^+$ and I is in the presence).

$$\mathrm{NRe(R_2PCH_2CH_2PR_2)_2Cl^+ + H_2O \rightleftharpoons NRe(R_2PCH_2CH_2PR_2)_2(H_2O)^{2+} + Cl^-} \qquad (4)$$

from both ^{31}P NMR and UV–visible spectral measurements that NRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl$^+$ is exclusively present in 0.09 M KCl or 0.09 M HCl. In general, such trans-effect equilibria must be dealt with in photophysical studies of metal–element multiple bonds.

Figure 4 displays a titration curve for NRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl$^+$ expressed as a plot of the efficiency of quenching by protonation (I/I_0) versus pH (I_0 is the intensity of emission in the absence of H$^+$ and I is in the presence). The quenching experiments were conducted in 0.1 M chloride media so as to keep the ionic strength constant. Although this curve has the form of a titration curve, it is clear that the transition zone corresponding to the "buffer" region is far broader than that found for a rapid protonation–deprotonation equilibrium. Apparently, kinetic features play a significant role in the excited-state protonation reaction.

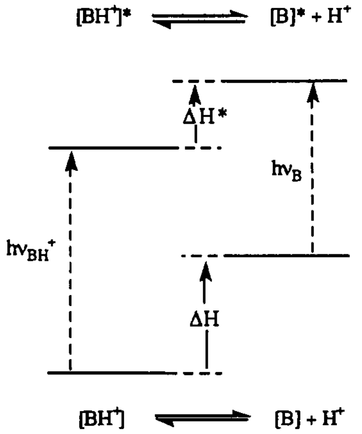
The changes in basicity (Δp*K*) between a ground (B and BH$^+$) and an excited (B* and BH^{+*} state can be estimated by the Forster cycle shown in Scheme I, where $h\nu_{BH^+}$ and $h\nu_B$ are the absorption energies for the initially populated *singlet* excited states of the protonated and deprotonated forms of the complex.[17] Note that these values are determined from the 0–0 transition. ΔH

---

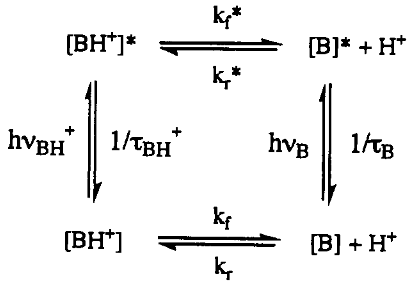
[16] These tenative spectral assignments are based on our assignments for NRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl$^+$ and related complexes[5a] and for other closely related oxo and nitrido species.

[17] Forster, Th. *Angew. Phys. Chem.* **1950**, *54*, 42, 531.

Scheme I



Scheme II



and ΔH^* refer to the enthalpy changes in the ground and excited states that occur upon protonation and are assumed to follow the relation $\Delta H \sim \Delta G = 2.303RT(\mathrm{p}K)$. In our case, because of rapid intersystem crossing due to spin–orbit coupling, the excited-state protonation will occur from a state that is predominantly triplet in character.[5c] From the thermodynamic cycle in Scheme I the relation $\Delta \mathrm{p}K = 0.00209\ (\nu_{\mathrm{B}} - \nu_{\mathrm{BH^+}})$ obtains at room temperature, where ν_{B} and $\nu_{\mathrm{BH^+}}$ are the 0–0 transition energies for the processes in Scheme I in cm^{-1}. With the limitation that the peak maxima of the $(d_{xy})^2 \rightarrow (d_{xz})^1(d_{yz})^1$ transition in both forms must be used instead of the 0–0 transition energies (362 and 408 nm), and the assumption that the singlet–triplet separation is constant for both forms, $\Delta\mathrm{p}K$ is 6.4. Thus, a $\mathrm{p}K^*$ of 5.4 is predicted, compared to the observed value of 4.5.

The kinetic case for our complex is shown in Scheme II,[8b] where k_f^* and k_r^* are the rate constants for the forward and reverse protonation reaction of the excited state, k_f and k_r are the rate constants for the forward and reverse protonation reaction of the ground state, $h\nu_{\mathrm{BH^+}}$ and $h\nu_{\mathrm{B}}$ signify the energies for the kinetically prompt excitation processes that populate the excited states of the protonated and deprotonated forms of the complex, and $\tau_{\mathrm{BH^+}}$ and τ_{B} are the lifetimes (s^{-1}) of the two excited forms. From consideration of the scheme, when $\tau_{\mathrm{BH^+}} = \tau_{\mathrm{B}}$ and $1/\tau_{\mathrm{B}} \ll k_r^*[\mathrm{H}^+]$, $1/\tau_{\mathrm{BH^+}} \ll k_f^*$, the excited states are in equilibrium with the proton pool. Practically this means that a luminescence titration will yield a "thermodynamic" value for $\mathrm{p}K^*$ and that the Forster equation should apply. In the case where $\tau_{\mathrm{BH^+}} \neq \tau_{\mathrm{B}}$ but excited-state protonation–deprotonation is rapid compared to the rate of excited-state decay, the luminescence titration will be displaced from the true $\mathrm{p}K^*$ value according to the relation $\mathrm{p}K^*(\mathrm{obs}) = \mathrm{p}K^* - \log(\tau_{\mathrm{BH^+}}/\tau_{\mathrm{B}})$. We note that the Forster calculation appears to seriously overestimate $\mathrm{p}K^*$ since the lack of observable emission for BH^+ likely indicates that $\tau_{\mathrm{BH^+}} < \tau_{\mathrm{B}}$ and that $\mathrm{p}K^*$ is actually less than $\mathrm{p}K^*(\mathrm{obs})$. The combination of the Forster equation and the kinetics shown in Scheme II yields only a qualitative and incomplete picture of the excited-state protonation reaction. Also, given the broad nature of the buffer zone, it is likely that either condition $1/\tau_{\mathrm{B}} \ll k_r^*[\mathrm{H}^+]$ or $1/\tau_{\mathrm{BH^+}} \ll k_f^*$ or both do not strictly apply.

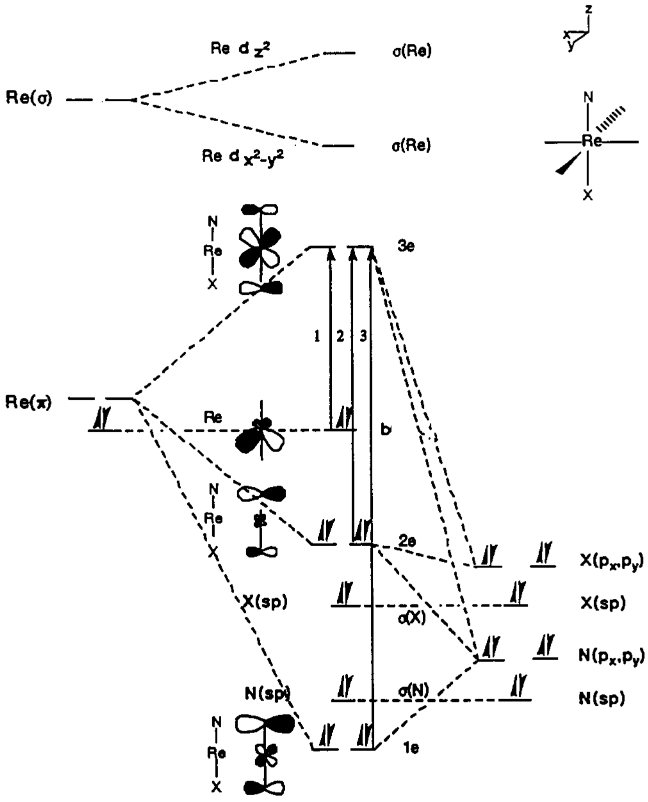


Figure 5. Simplified molecular orbital diagram for $\mathrm{NRe(Me_2PCH_2CH_2PMe_2)_2Cl^+}$, which assumes C_{4v} symmetry. Note that the lowest energy transition (1) is predicted to be between metal-localized orbitals (see text) while the next two have substantial charge-transfer character.

That the excited-state protonation is dependent upon the composition of the coordination sphere around the $\mathrm{ReN^{2+}}$ core is demonstrated by the luminescence titration (by quenching) shown in Figure 4 for *trans*-$\mathrm{NRe(CN)_4(H_2O)^{2-}}$. Here, a plot of I/I_0 versus pH behaves in a more "normal" fashion, revealing a buffer zone that changes over ca. 2 pH units. The apparent $\mathrm{p}K^*(\mathrm{obs})$ is 3.6, and as for the dmpe complex, no emission from the protonated form is seen to ca. 850 nm. Thus, despite the overall negative charge of the complex, the cyano-rich coordination sphere results in a weaker excited-state basicity than that of the phosphine-rich dmpe complex. Attempted ground-state titration gave unsatisfactory results presumably because of the existence of multiple protonation equilibria involving the cyano groups.

Comparison of Excited- and Ground-State Basicities for $\mathrm{NRe(Me_2PCH_2CH_2PMe_2)_2Cl^+}$. It is apparent that the excited state of $\mathrm{NRe(Me_2PCH_2CH_2PMe_2)_2Cl^+}$ is far more basic than the ground state. The behavior of the excited $\mathrm{ReN^{2+}}$ core can be rationalized in a qualitative fashion by the orbital diagram shown in Figure 5, where it is seen that excitation from the essentially metal-localized b (d_{xy}) orbital to the *e* (d_{xy}, d_{yz}) set (in C_{4v} symmetry) results in lowering the Re–N bond order while placing electron density on nitrogen relative to the ground state.[18] Chemical effects of increased basicity in the excited states of metal oxo and metal alkylidyne complexes have been observed previously, and our work extends this to metal nitrides. A future goal is to provide an isoelectronic, isostructural series of metal–element multiple bonds where changes in excited-state basicity, and nucleophilicity, can be studied at a common metal center within the same coordination environment.

Acknowledgment. The authors thank Jon Caspar of Du Pont and Wayne Jones of The University of North Carolina for excited-state-lifetime measurements. B.P.S. thanks Harry Gray for discussions that resulted in this work. NSF support under the EPSCoR program is gratefully acknowledged.

---

[18] Dubois, D. L.; Hoffman, R. *New J. Chem.* **1977**, *1*, 479.