been proposed to bind through a hydrogen bond between the hydroxy group of the intercalators and the C2 carbonyl oxygen of the thymine ring. Extended Hückel molecular orbital calculations for adenine, guanine, hypoxanthine, cytosine, and uracil indicated that the amino substituent supplies electrons to the π orbital of the purine and pyrimidine rings and raises the highest occupied molecular orbital (HOMO) energy level, while the electrons from the carbonyl group occupy the nonbonding orbital.[24] The result further indicates that the presence of an amino group tends to decrease the energy difference between the HOMO of NMP and the lowest unoccupied molecular orbital (LUMO) of Pt(L)(en), favoring the charge transfer between the two rings.[25]

The present findings add to information relevant to thermodynamic selectivity and structure-dependent weak forces that could lead to molecular recognition involving nucleotides[26] and site-specific DNA cleavage reactions.[27]

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Supplementary Material Available: Table listing ^{13}C NMR chemical shifts (δ_c) and upfield shifts ($\Delta\delta$) of NMP for 0.05 M NMP–Pt(Me$_2$phen)(en) at 70 °C (1 page). Ordering information is given on any current masthead page.

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Department of Chemistry
Faculty of Science
Nagoya University
Chikusa-ku, Nagoya 464-01, Japan

Akira Odani
Hideki Masuda
Osamu Yamauchi*

Department of Electronic Chemistry
Tokyo Institute of Technology at Nagatsuta
Yokohama 227, Japan

Shin-ichi Ishiguro

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Luminescent Nitridorhenium(V) Complexes

Although photochemical and photophysical studies of transition-metal–main-group complexes containing multiple bonds have been confined primarily to metal–oxo derivatives,[1] there should exist an extensive excited-state chemistry of complexes containing metal–nitrogen multiple bonds. Study of these complexes promises to increase our understanding of the electronic structure of the multiple bond and, in a more practical sense, result in new materials for energy conversion and small-molecule transformation. In our efforts to discover new excited states we have prepared a series of new complexes of the type *trans*-$NRe(R_2PCH_2CH_2PR_2)_2X^+$ (R = Me, X = Cl, Br; R = Et, X = Cl), which are the first rhenium nitrido complexes to exhibit fluid-solution luminescence at room temperature. These desirable emission properties provide a convenient kinetic handle for exploration of their photophysics. An early lead in our work was provided by several studies on the excited-state properties of nitridoosmium(VI) complexes.[2,3]

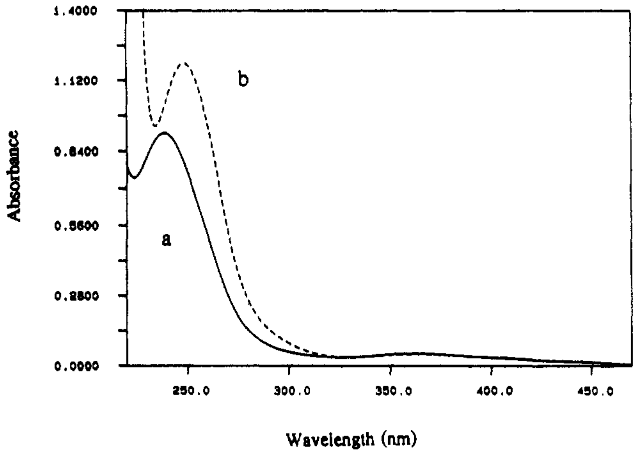

Figure 1. Electronic spectrum for [*trans*-NRe(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Cl]Cl in water (a) and after addition of 0.1 M KBr (b) to the same solution.

Preparation of *trans*-$NRe(R_2PCH_2CH_2PR_2)_2Cl^+$ (R = Me, Et) is accomplished by direct interaction of the reactive precursor $NRe(PPh_3)_2Cl_2$[4,5] with the appropriate diphosphine ligand in a manner similar to that of Johnson[6] (eq 1). Isolation as the

$$NRe(PPh_3)_2Cl_2 + 2[R_2PCH_2CH_2PR_2] \xrightarrow{\text{EtOH, heat}} NRe(R_2PCH_2CH_2PR_2)_2Cl^+ + 2PPh_3 + 2Cl^- \quad (1)$$

chloride or hexafluorophosphate salts followed by crystallization from CH_2Cl_2/Et_2O or $CH_3CN/CH_3C_6H_5$ mixtures results in pale yellow to yellow microcrystalline samples[7] that luminesce brilliant green in the solid state. ^{31}P and ^{1}H NMR and infrared spectral data, in addition to elemental analyses, support the formulations of the complexes.[8]

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(8) Characterization data for [*trans*-$NRe(Me_2PCH_2CH_2PMe_2)_2Cl]^+$ are as follows. UV–visible spectrum in CH_2Cl_2: λ_{max} = 238 nm (ϵ = 4000 $M^{-1}cm^{-1}$), λ_{sh} = 257 nm (ϵ = 2980 M^{-1} cm^{-1}), λ_{max} = 362 nm (ϵ = 250 M^{-1} cm^{-1}). Infrared spectrum in CH_2Cl_2: ν(Re–N) = 1059 cm^{-1}. ^{1}H NMR spectrum in CD_3CN in ppm, δ: 1.70 (3 H, s, br), 2.00 (3 H, s, br), 2.07 (4 H, t). ^{31}P NMR spectrum in CD_3CN: 17.4 ppm vs H_3PO_4. Anal. Calcd for $[NRe(Me_2PCH_2CH_2PMe_2)_2Cl](PF_6)$: C, 21.16; H, 4.75; N, 2.06. Found: C, 21.38; H, 4.72; N, 1.91. The ^{1}H NMR spectrum revealed a small fraction of toluene present in some samples.

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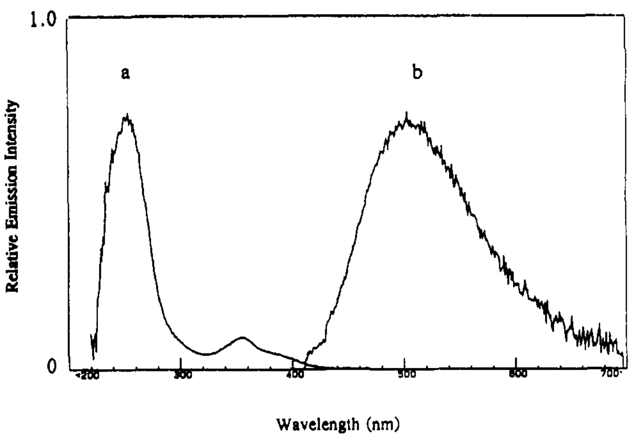

Figure 2. Excitation spectrum (507-nm monitoring wavelength; a) and emission spectrum (360-nm excitation wavelength; b) of [*trans*-NRe($Et_2PCH_2CH_2PEt_2$)$_2$Cl]PF_6 recorded in CH_3CN solution.

The chloro complexes exchange with other anionic ligands such as Br^-, I^-, or N_3^- in polar solvents (eq 2) with half-lives on the

$$NRe(R_2PCH_2CH_2PR_2)_2Cl^+ + Br^- \rightleftharpoons NRe(R_2PCH_2CH_2PR_2)_2Br^+ + Cl^- \quad (2)$$

order of seconds in water. The equilibrium depicted in eq 2 can be exploited for preparative purposes. For example, reaction of *trans*-NRe($Me_2PCH_2CH_2PMe_2$)$_2Cl^+$ with KN_3 in $MeOH/H_2O$ produces the azido derivative *trans*-NRe($Me_2PCH_2CH_2PMe_2$)$_2N_3^+$ in good yield. Figure 1 shows the electronic spectrum of *trans*-NRe($Me_2PCH_2CH_2PMe_2$)$_2Cl^+$ in water before and after the addition of an excess of KBr. The exchange process is dramatically reflected by a change in both the band shape and maxima of transitions centered at ca. 240 nm. The presence of a ligand dissociation process is demonstrated by an increase in absorptivity with added Cl^- for the chloro complex *trans*-NRe($Me_2PCH_2CH_2PMe_2$)$_2Cl^+$ in water corresponding to the production of a limiting form. Consistent with this conclusion ϵ_{max} values as a function of concentration are decidedly nonlinear in water. In less polar solvents like CH_2Cl_2 and CH_3CN the dissociation appears to be less important; for example, extinction coefficient data are not concentration dependent for *trans*-NRe($Me_2PCH_2CH_2PMe_2$)$_2X^+$ ($X = Cl^-, Br^-$) and the addition of (n-C_4H_9)$_4$NBr to solutions of *trans*-NRe($Me_2PCH_2CH_2PMe_2$)$_2Br^+$ produces no spectral changes.

As shown in Figure 1, the electronic spectra of *trans*-NRe($Me_2PCH_2CH_2PMe_2$)$_2X^+$ ($X = Cl^-, Br^-$) exhibit two band systems, one of moderate intensity (ϵ_{max} is 3800–4500) near 240 nm and a weaker one (ϵ_{max} is 250–410) at ca. 361 nm. Comparison of electronic spectral data in aqueous solution containing excess X^- for a series of derivatives where $X^- = Cl^-$ (240 nm), Br^- (248 nm), N_3^- (262 nm), and I^- (264 nm) shows that the position of the high-energy band system is strongly dependent on the identity of the axial ligand whereas the position of the lower energy band system is constant at 361 ± 2 nm. From these results we assign the latter transition as "ligand field" and the former as ligand (X^-) to metal charge transfer (LMCT). The assignment of the transitions can be made on the basis of qualitative electronic structural arguments[9] and on previous assignments for $NOs^{VI}X_4^-$ and $Re^VO_2(py)_4^+$,[1,2] that is, two closely spaced ligand field transitions ($a_1 \rightarrow b_1$, $a_1 \rightarrow b_2$) and two LMCT transitions ($b_1 \rightarrow b_1$, $b_2 \rightarrow b_2$). In C_{2v} symmetry the $d_{x^2-y^2}$ (a_1) orbital is essentially nonbonding, while the d_{xz} (b_1) and d_{yz} (b_2) orbitals will contain $X(p_x)$, $N(p_x)$ and $X(p_y)$, $N(p_y)$ character, respectively, in an antibonding fashion.

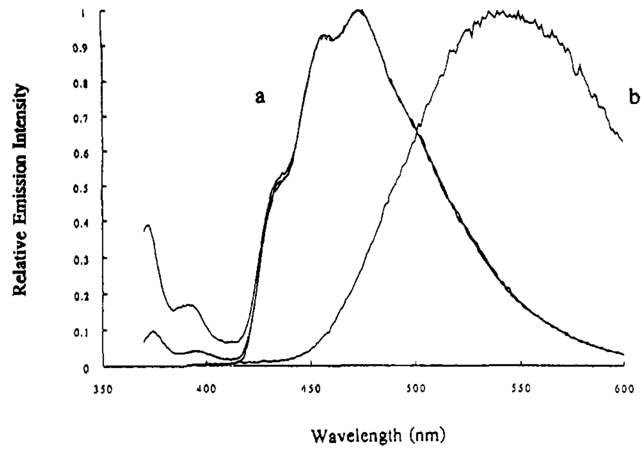

Figure 3. Emission spectrum of [*trans*-NRe($Et_2PCH_2CH_2PEt_2$)$_2$Cl]PF_6 recorded at 77 K in a 4:1 EtOH/MeOH glass (a). The three spectra represent excitation at 330, 350, and 370 nm. Spectrum b is at room temperature in the same solvent mixture. Note the vibronic structure at 77 K, but the loss of structure and large red shift upon warming to room temperature (see text).

Table I. Excited-State Properties of *trans*-[NRe($Me_2PCH_2CH_2PMe_2$)$_2$Cl]$^+$ in Various Solvents[a]

solvent	E_{em}, nm	τ_{em}, μs[b]	ϕ_{em}[c]	AN[d]	D_s[e]
CH_2Cl_2	508	0.34	0.0007	20.1	9.1
CH_3CN	504	0.36	0.0012	19.3	36.0
C_2H_5OH	528		0.0035	33.5	29.0
CH_3OH	530	1.93	0.0037	37.1	35.9
H_2O	539[f]	1.66[g]	0.0032	54.8	80.1

[a] Measured at 20 °C in deoxygenated solvents as the PF_6^- salt. [b] Radiative lifetime. [c] Quantum yield of emission. [d] Acceptor number; see ref 10. [e] Static dielectric constant. [f] Measured in the presence of LiCl. [g] In pure water; multiexponential decay; lifetime is the single exponential fit.

Figure 2 shows emission and excitation spectra of *trans*-NRe($Et_2PCH_2CH_2PEt_2$)$_2Cl^+$ in CH_3CN solution at room temperature. Under these conditions both *trans*-NRe($Et_2PCH_2CH_2PEt_2$)$_2Cl^+$ and *trans*-NRe($Me_2PCH_2CH_2PMe_2$)$_2Cl^+$ exhibit structureless emission, which occurs at ca. 507 nm (±5 nm). At 77 K in 4:1 EtOH/MeOH glass *trans*-NRe($Et_2PCH_2CH_2PEt_2$)$_2Cl^+$ exhibits a highly structured emission showing four vibronic components (Figure 3). The vibrational structure has an average spacing of 1060 cm^{-1} and maximum intensity for the (0–2) transition, both implicating an electronic transition involving a highly distorted rhenium–nitrogen mode. This observation supports the assignment that the emission process is a complement of the low-energy absorption processes, i.e., a transition involving orbitals which result in a change in the Re–N π-bond order.

Lifetime measurements on both complexes show values in the range 300–2000 ns depending on the solvent, which is characteristic of transition-metal-based excited states that are predominantly "triplet" in nature. Table I gives values for emission energies, lifetimes, and quantum yields for *trans*-NRe($Me_2PCH_2CH_2PMe_2$)$_2Cl^+$ in a number of solvents of different solvation properties. As seen in the table, the variation of the emission maximum (E_{em}) with solvent is large, changing by 0.16 V from CH_3CN to water. The emission energy is found to decrease as the acceptor number (AN)[10] of the solvent increases. The trend with solvent can be interpreted as stabilization of the thermally equilibrated excited state by acceptor properties of the solvent. This can occur if the excited-state electron distribution

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(9) For $NOs^{VI}Cl_4^-$ and $NOs^{VI}(NH_3)_4^{3+}$ the orbital ordering in C_{4v} symmetry is $b_2(d_{xy}) < e(d_{xz},d_{yz}) < b_1(d_{x^2-y^2}) < a_1(d_{z^2})$. For *trans*-$O_2Re(py)_4^+$, which is D_{4h}, the orbital ordering is the same, i.e., $b_{2g} < e_g < b_{1g} < a_{1g}$. For the strictly C_{2v} symmetry *trans*-NRe($R_2PCH_2CH_2PR_2$)$_2X^+$ complexes the formal orbital labels with change because the molecular and symmetry axes are noncoincident. For this case the nonbonding π-type orbital is $d_{x^2-y^2}$ and the π-bonding orbitals (d_{xz}, d_{yz}) are formally nondegenerate. Considering the nature of the diphosphine, these π-bonding orbitals should be closely spaced.

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is such that the nitrido ligand is electron-rich relative to the ground state. An explanation based on stabilization of a charge-separated excited state by a dielectric continuum can be rejected, since the static dielectric constant (D_s) does not correlate with E_{em}.

Since the quantum yield of emission of *trans*-[NRe($Me_2PCH_2CH_2PMe_2)_2Cl]^+$ is generally <0.004 for the solvents in question, the excited-state lifetime is controlled by radiationless decay processes. Although quantitative data are not yet available, it is clear from the absorption spectral changes which accompany prolonged irradiation that a photochemical reaction channel competes with radiative decay. The decrease in lifetime as the excited-state energy increases may be due to more effective thermal population of a higher lying reactive state. This may prove an important point in the eventual understanding of the photochemistry of metal-multiple-bonded complexes.

Preliminary cyclic voltammetry studies show that *trans*-$NRe(Et_2PCH_2CH_2PEt_2)_2Cl^+$ possesses a quasireversible (i_{pa}/i_{pc} = 0.30) oxidation at +1.5 V (SCE, CH_3CN/0.1 M tetra-*n*-butylammonium hexafluorophosphate, 100 mV/s sweep rate) that is coupled to the formation of a product at E_p = 1.0 V and a large multielectron irreversible reduction at E_p = −1.9 V. These data allow a rough estimate of the one-electron redox potentials of the excited state to be made. For the *trans*-$NRe(Et_2PCH_2CH32PEt_2)_2Cl^{+,*/0}$ couple this is +0.4 V, while for *trans*-$NRe(Et_2PCH_2CH_2PEt_2)_2Cl^{2+/+,*}$ this is −0.8 V. Our future studies are focused on the exploration of these excited-state redox properties, the implied atom transfer properties, and the understanding of the relationship of the photochemical pathway to these.

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Registry No. *trans*-$NRe(Et_2PCH_2CH_2PEt_2)_2Cl^+$, 136838-66-9; *trans*-$NRe(Me_2PCH_2CH_2PMe_2)_2Cl^+$, 136838-67-0; *trans*-$NRe(Me_2PCH_2CH_2PMe_2)_2Br^+$, 136838-68-1; CH_2Cl_2, 75-09-2; CH_3CN, 75-05-8; C_2H_5OH, 64-17-5; CH_3OH, 67-56-1; H_2O, 7732-18-5.

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

Gregory A. Neyhart
Kevin J. Seward
James Boaz
B. Patrick Sullivan*

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Reactions at Metal-Bound Nitrogen Atoms. Synthesis and Structure of $V(NPMePh_2)Cl_4(NCMe)\cdot MeCN$

We have been exploring the synthesis and chemistry of complexes with silyl-substituted imido ligands in order to use the nitrogen–silicon bond as a reactive site for formation of nitride-bridged transition-metal compounds and materials.[1-3] In order to understand in a general sense the range of reactivity available to silylimido derivatives, their chemistry with a variety of reagents capable of attacking the silylimido ligand is being examined. We report here reactions of $V(NSiMe_3)Cl_3$[1a,4] (**1**) with PCl_2MePh_2 and Cl_2 which result in unusual transformations of the silylimido ligand into phosphiniminato and chloroimido ligands, respectively.

Addition of 1 equiv of PCl_2MePh_2 to **1** in dichloromethane results in rapid elimination of 1 equiv of $ClSiMe_3$ and quantitative formation of a vanadium(V) phosphiniminato compound, $V(NPMePh_2)Cl_4$ (**2**) (eq 1). The ^1H NMR spectrum of **2** shows

$$\underset{\mathbf{1}}{\mathrm{V(NSiMe_3)Cl_3}} \xrightarrow[-\,\mathrm{ClSiMe_3}]{+\,\mathrm{PCl_2MePh_2}} \underset{\mathbf{2}}{\mathrm{V(NPMePh_2)Cl_4}} \xrightarrow{+\,\mathrm{L}} \underset{\mathbf{3}}{\mathrm{V(NPMePh_2)Cl_4(L)}} \quad (1)$$

a doublet for the phosphiniminato methyl protons with a chemical shift (δ 2.88) and a proton–phosphorus coupling constant (J = 12 Hz) in the range we have found to be characteristic of methyl groups attached to the phosphorus(V) of phosphiniminato ligands.[5] The ^{31}P NMR chemical shift for **2** (δ 58) is likewise in the region expected,[5] although this signal is unusually broad ($\nu_{1/2}$ = 600 Hz) as the result of unresolved coupling of the phosphorus to nitrogen and vanadium.[6] Compound **2** is isolated from cold dichloromethane in 75% yield as an air-sensitive maroon crystalline solvate, $V(NPMePh_2)Cl_4\cdot{}^1/_2CH_2Cl_2$. The IR spectrum of this solid exhibits a strong absorption at 1120 cm^{-1} assigned to the asymmetric VNP vibration and characteristic of phosphiniminato complexes.[7] The solid-state structure of **2** is not known, but by analogy to the related niobium and tantalum phosphiniminato complexes, $[Nb(NPPh_3)Cl_4]_2\cdot CH_2Cl_2$[8] and $[Ta(NPPh_3)Cl_4]_2$,[9] we expect that **2** is a chloro-bridged dimer.

Coordinating solvents readily add to **2**, producing adducts $V(NPMePh_2)Cl_4(L)$, where L = MeCN (**3a**), THF (**3b**), or pyridine (**3c**) (eq 1). Compound **3a** crystallizes from acetonitrile as a monosolvate, $V(NPMePh_2)Cl_4(NCMe)\cdot MeCN$, for which the solid-state structure has been determined by X-ray diffraction.[10] There are two independent six-coordinate molecules of **3a** per asymmetric unit (Figure 1). Their V–N(phosphiniminato) distances, V(1)–N(1) = 1.653 (3) Å and V(2)–N(3) = 1.656 (3) Å, are the same within experimental error and in the range of V–N distances reported for vanadium(V) imido compounds.[11a] The short V–N(phosphiniminato) distances suggest substantial vanadium–nitrogen π-bonding, consistent with a triple bond. Distortions from idealized octahedral geometry further support this idea: the cis chlorides are bent away from the phosphiniminato ligand and the elongated V–N(acetonitrile) distances suggest a significant trans influence.[11b] The N–P distances, N(1)–P(1) = 1.660 (3) Å and N(3)–P(2) = 1.667 (3) Å, are typical of those observed for phosphiniminato ligands,[5,7] midway between the values quoted for N–P single and double bonds.[12] This is usually interpreted as indicating phosphorus–nitrogen π-bonding;[7] however, the shortened N–P distances can also be rationalized as arising from the sp hybridization of the nitrogen atoms.[13] The VNP angles differ somewhat between the two independent molecules of **3a** (V(1)–N(1)–P(1) = 171.8 (2)° and V(2)–N-

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