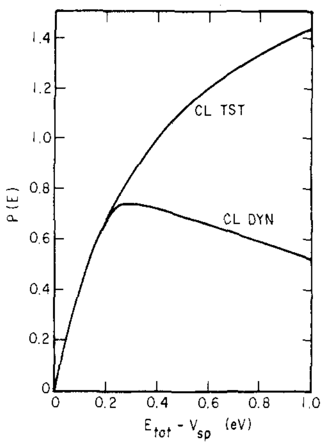

Figure 1. Reaction probability for the collinear $H + H_2$ reaction on the Porter-Karplus potential surface from a microcanonical classical trajectory calculation (CL DYN) and microcanonical classical transition state theory (CL TST), as a function of total energy above the barrier height (1 eV = 23.06 kcal/mol).

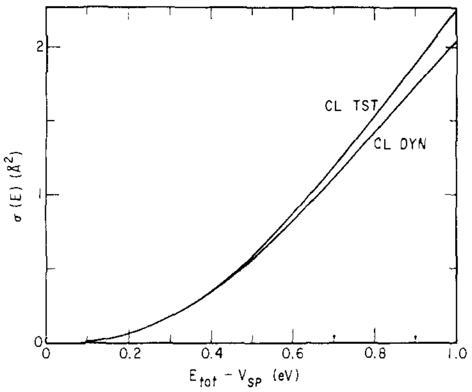

Figure 2. Same as Figure 1, except that $\sigma(E)$ is the reactive cross section for the three-dimensional $H + H_2$ reaction.

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(1) See, for example, R. Wolfgang, *Acc. Chem. Res.*, **2**, 248 (1969).
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Reversible Electron Transfer to the Nitrosyl Group in Ruthenium Nitrosyl Complexes

Sir:

In transition metal nitrosyl complexes the electronic distribution in the metal-nitrosyl bond and the assignment of formal oxidation states, remain areas of some controversy.[1] However, in an appropriate coordination environment (one in which the ν(NO) stretching frequency is relatively high) the nitrosyl group has been shown to react chemically as the nitrosonium ion (NO^+).[2-10] The nitrosyl group in complexes like *cis*-$Ru(bipy)_2(NO)Cl^{2+}$ (bipy is 2,2′-bipyridine) reacts with nucleophiles like OH^- and N_3^-,[2,3] diazotizes primary amines,[7] and acts as an electrophile in aromatic substitution reactions.[8]

The free nitrosonium ion is also a strong oxidant.[11,12] Although the nitrosyl group has been reported to act as an oxidant in net redox reactions,[13-15] with the exception of nitroprusside ion,[16] the reactions do not involve simple electron transfer. We have prepared the series of nitrosyl complexes $[Ru(bipy)_2(NO)A]^{3+}$ (A is N_3^-, Cl^-,[2] NO_2^-, NH_3, py,[2] and CH_3CN). From voltammetry and cyclic voltammetry experiments at a platinum bead electrode, we find that the nitrosyl complexes undergo electrochemically reversible one-electron reduction reactions in acetonitrile in the potential range 0.2-0.6 V (*vs.* the saturated sodium chloride calomel electrode at 25 ± 2°), and a second irreversible one-electron reduction at more cathodic potentials. ν(NO) and voltammetric $E_{1/2}$ values are dependent upon the ligand A cis to the nitrosyl group in a systematic way: for $Ru(bipy)_2(NO)Cl^{2+}$, $E_{1/2} = 0.20$ V, $\nu(NO) = 1940$ cm^{-1} (in acetonitrile); for $Ru(bipy)_2(NO)(CH_3CN)^{3+}$, $E_{1/2} = 0.56$ V, $\nu(NO) = 1970$ cm^{-1} (in acetonitrile).

The nitrosyl complexes can be reduced chemically (using I^- as reductant) or electrochemically ($n = 1.00 \pm 0.05$) to give one-electron reduction products, e.g., $Ru(bipy)_2(NO)Cl^+$ and $Ru(bipy)_2(NO)(CH_3CN)^{2+}$. In deaerated acetonitrile, acetone, or water solutions the reduction products are stable indefinitely; however, they do react slowly with oxygen in solution. The stable black iodide salt, $[Ru(bipy)_2(NO)Cl]I$, which gives excellent elemental analyses,[17] has been isolated in good yield.

The results of several experiments show that the electron transfer properties of the nitrosyl complexes are carried mainly by the nitrosyl ligand. (1) Upon reduction ν(NO) shifts dramatically to lower energies (1650 cm^{-1} for $Ru(bipy)_2(NO)(CH_3CN)^{2+}$ and 1610 cm^{-1} for $Ru(bipy)_2(NO)Cl^+$) as shown by ^{15}N labeling studies. The magnitude of the shifts in ν(NO), ~300 cm^{-1}, are in the same range as when NO^+ is reduced to NO.[4] (2) In contrast to normal bis(2,2′-bipyridine)ruthenium(III)/(II) couples, $E_{1/2}$ values for the nitrosyl complexes are sensitive to medium effects. In acetonitrile, $E_{1/2}$ for the $[Ru(bipy)_2(NO)Cl]^{2+/+}$ couple shifts 0.1 V to a lower potential when the supporting electrolyte is changed from 0.1 *M* $N(n\text{-}C_4H_9)_4PF_6$ to 0.1 *M* $LiClO_4$. Specific medium effects might be expected if electron transfer occurs to and from a group on the periphery of the complex rather than to and from metal d orbitals. (3) The epr spectrum of $[Ru(bipy)_2(NO)Cl]^+$ in frozen acetone at 170°K is qualitatively identical with the frozen solution spectrum of the one-electron reduced nitroprusside ion, $Fe(CN)_5NO^{3-}$.[18a] For both $Fe(CN)_5NO^{3-}$ and $Ru(bipy)_2(NO)Cl^+$ the expected ^{14}N hyperfine splittings are observed. In neither case has evidence been found for metal hyperfine interactions. The epr results and the results of a magnetically perturbed Mössbauer study on $[Fe(CN)_5NO]^{3-}$ [19] show that the unpaired spin density is confined largely to the nitrosyl ligand. This is in marked contrast to $[Fe(CN)_4NO]^{2-}$ where a large ^{57}Fe hyperfine interaction has been observed ($A_{ISO} = -7.21$ G) and the unpaired electron appears to be localized largely on the metal.[18]

The similarities between nitroprusside ion and the ruthenium nitrosyl complexes indicate that the molecular orbital scheme developed by Manoharan and Gray for the nitroprusside ion[20] is also appropriate for the ruthenium nitrosyl complexes. In that scheme the lowest unoccupied molecular orbital is largely $\pi^*(NO)$ in character with some metal d character.

The ruthenium nitrosyl complexes provide an unusual example where simple electron transfer occurs to and from a coordinated ligand. The nitrosyl complexes are moderately strong oxidants whose reduction potentials fall in a range which overlaps the potentials for closely related Ru(III)/Ru(II) couples (e.g., $Ru(bipy)_2Cl_2^{+/0}$ at 0.32 V). The nitrosyl complexes undergo facile electron transfer. From stopped flow measurements at 25° in acetonitrile, the reaction

$$\begin{aligned} &Ru(bipy)_2Cl_2 + Ru(bipy)_2(NO)(CH_3CN)^{3+} \longrightarrow \\ &\qquad Ru(bipy)_2Cl_2^{+} + Ru(bipy)_2(NO)(CH_3CN)^{2+} \\ &\qquad \Delta\mathcal{E} \doteq 0.26\ \mathrm{V} \end{aligned}$$

occurs with $k > 10^6\ M^{-1}\ \mathrm{sec}^{-1}$ (assuming that the reaction is second order). By observing the appearance of $\nu(^{14}NO)$ (1940 cm^{-1}) and the disappearance of $\nu(^{15}NO)$ (1900 cm^{-1}) in the region 1860–1970 cm^{-1} in acetonitrile, we estimate that for the self-exchange reaction

$$\begin{aligned} &Ru(bipy)_2(^{14}NO)Cl^{+} + Ru(bipy)_2(^{15}NO)Cl^{2+} \longrightarrow \\ &\qquad Ru(bipy)_2(^{14}NO)Cl^{2+} + Ru(bipy)_2(^{15}NO)Cl^{+} \end{aligned}$$

$k > 10^2\ M^{-1}\ \mathrm{sec}^{-1}$, at room temperature.

We recently reported that efficient, light-catalyzed, net intramolecular electron transfer occurs between Ru(III) and coordinated azide ion[21]

$$\begin{aligned} &Ru(bipy)_2(N_3)_2^{+} + CH_3CN \xrightarrow{h\nu} \\ &\qquad Ru(bipy)_2(CH_3CN)(N_3)^{+} + \tfrac{3}{2}N_2 \end{aligned}$$

It is interesting to note that in the nitrosyl complexes the roles of ligand and metal can apparently be reversed. Upon uv irradiation a seemingly efficient, light-induced reaction occurs (eq 1) which is quantitative as shown by gas evolution and spectral studies. At least in the formal sense, reac-

$$\begin{aligned} &Ru^{II}(bipy)_2(\overset{+}{N}O)Cl^{2+} + CH_3CN \xrightarrow{312\ \mathrm{nm}} \\ &\qquad Ru^{III}(bipy)_2(CH_3CN)Cl^{2+} + NO \qquad (1) \end{aligned}$$

tion 1 involves net electron transfer from ruthenium to the nitrosyl group.

The redox properties of the nitrosyl complexes reinforce the idea that, in an appropriate coordination environment, the nitrosyl group can be adequately described as a chemically modified form of the nitrosonium ion. The nitrosyl complexes reported here are potentially versatile electron transfer reagents with synthetically controllable reduction potentials and have low kinetic barriers to electron transfer.

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Generation of Boracarbenoid and Boracyclopropene Intermediates from the Photolysis of Tetraorganoborate Salts in Aprotic Media[1]

Sir:

The photolysis of tetraarylborate salts in protic media, under anaerobic[2,3] or aerobic[3] conditions, has led to novel dihydrobiaryl or biaryl coupling products, respectively. As an extension of our interest in chemically induced 1,2-aryl shifts from boron to carbon,[4] we have been led to examine such rearrangements initiated photochemically under aprotic conditions and under nitrogen. By avoidance of hydroxylic solvents we hoped to generate and detect the potentially interesting boron fragments and rings thought to be involved in these photochemical processes.

We now wish to report that the irradiation at 254 nm of sodium tetraphenylborate(III) (**1**) in anhydrous tetrahydrofuran or 1,2-dimethoxyethane causes two principal photoreactions: (a) the direct formation of biphenyl (**2**) and a solution reagent having the properties of sodium diphenylborate(I) (**3**) and (b) the generation of a mixture of sodium arylborohydrides(III) (**4**), where the aryl group can be phenyl, biphenylyl, and *m*- or *p*-terphenylyl groups (Scheme I). Furthermore, in the course of characterizing these reaction pathways, we have uncovered evidence that sodium diphenylborate(I) (**3**), whose anion is isoelectronic with a carbene, does behave in a carbenoid fashion toward diphenylacetylene. Generation of **3** by irradiation of **1** in DME and in the presence of diphenylacetylene and subsequent treatment