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Communications to the Editor

Photoreactivity of the Ruthenium Nitrosyl Complex, Ru(salen)(Cl)(NO). Solvent Effects on the Back Reaction of NO with the Lewis Acid Ru^{III}(salen)(Cl)[1]

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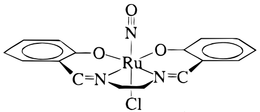
Nitric oxide has been broadly established as having important roles in mammalian biology as a bioregulatory molecule and as a toxic agent produced in immune response to pathogen invasion.[2] Furthermore, numerous disease states have been coupled to the over- or under-production of NO.[3] In this context, ongoing studies here have been concerned with the preparation and mechanistic evaluation of compounds potentially usable for photochemically activated delivery of NO to specific physiological targets.[4] Among such compounds have been various metal nitrosyl complexes, including those of ruthenium porphyrins[5] and ammines,[6] which are thermally stable yet are photochemically active toward NO release.[7] In this context, we have begun to explore a different synthetic platform for ruthenium nitrosyls, namely, the salen-type complexes Ru(R-salen)(X)(NO) where R-salen is a derivative of the *N*,*N*′-bis(salicylidene)ethylenediamine dianion. Additional interest in the nitrosyl ruthenium salen complexes derives from recent demonstrations that these are precursors of oxene and carbene transfer catalysts for the asymmetric epoxidations and cyclopropanations of alkenes as well as of Lewis acid catalysts for asymmetric hetero-Diels−Alder reactions.[8,9] These catalysts are reportedly activated by light,[8] so quantitative evaluation of their photochemical properties has multidimensional interest. Described here is the photoreactivity of a representative member of this family, Ru(salen)(Cl)(NO) (**1,** chloro(nitrosyl)(*N*,*N*′-bis(salicylidene)ethylenediaminato)ruthenium(II)) in various media. These results demonstrate the NO is photolabilized (reversibly) to give solvento ruthenium(III) analogues and provide a logical model to explain the photochemical activation and solvent-dependent reactivities of the catalysts noted above.



(**1**)

The optical spectrum of Ru(salen)(Cl)(NO)[10] displays a band at λ_{max} 384 nm ($\epsilon = 6.3 \times 10^3$ M^{-1} cm^{-1}) in tetrahydrofuran, and the FTIR spectrum shows a NO stretch at $\nu_{NO} = 1844$ cm^{-1} (dichloromethane). When a solution of **1** in THF was irradiated with 365 nm light, a new species was formed with UV−vis bands at 354 ($\epsilon = 1.1 \times 10^4$ M^{-1} cm^{-1}), 376 (1.2×10^4), 404 (1.4×10^4), and 516 nm (1.8×10^3) (isosbestic point at 325 nm). In addition, a broad band centered at 646 nm (3.3×10^3), assigned as a ligand (phenoxo) to metal (Ru^{III}) charge transfer (LMCT) band characteristic of Ru(III) salen complexes,[11] was also seen. The spectrum of the photoproduct and its decay back to that of **1** are shown in Figure 1. Similar spectral changes were seen with deaerated solutions of **1** (5×10^{-5} M) in acetonitrile and CH_2Cl_2 as well as in aerated toluene (the air was present to trap the NO generated). The IR spectra of product solutions showed disappearance of the ν_{NO} band and shifts to lower frequencies of the salen bands consistent with NO photodissociation. Neither chloride nor chlorine atom photodissociation would explain the

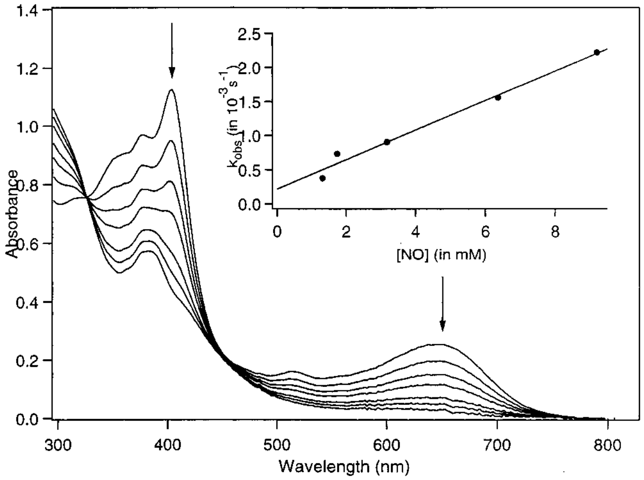


Figure 1. Temporal spectral changes following the reaction of photochemically generated Ru(salen)(Cl)(Sol) (**2**) with NO (9.2 mM) to regenerate Ru(salen)(Cl)(NO) (**1**) in THF. The spectra were recorded at intervals of 0, 150, 300, 450, 750, 1050, and 4380 s. The first of these (0 s), that with the highest absorbances at the λ_{max} indicated by the arrows, was recorded immediately after terminating the photolysis. Inset: Plot of k_{obs} vs [NO] for the reaction of **2** with NO in THF solution at 23 °C. The slope (k_{NO}) = 0.22 M^{-1} s^{-1} under these conditions.

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[1] Reported in part at the 217th National Meeting of the American Chemical Society, Anaheim, CA, March 1999, INORG 164.

[2] (a) Moncada, S.; Palmer, R. M. J.; Higgs, E. A. *Pharmacol. Rev.* **1991**, *43*, 109−142. (b) Feldman, P. L.; Griffith, O. W.; Stuehr, D. J. *Chem. Eng. News* **1993**, *71*, 10, 26−38. (c) Wink, D. A.; Hanbauer, I.; Grisham, M. B.; Laval, F.; Nims, R. W.; Laval, J.; Cook, J.; Pacelli, R.; Liebmann, J.; Krishna, M.; Ford, P. C.; Mitchell, J. B. *Curr. Top. Cell. Regul.* **1996**, *34*, 159−187. (d) Feelish, M.; Stamler, J. S., Eds. *Methods in Nitric Oxide Research*: John Wiley and Sons: Chichester, England, 1996, and references therein.

[3] E.g.: (a) Wiseman, H.; Halliwell, B. *Biochem. J.* **1996**, *313*, 17−29. (b) Wink, D. A.; Vodovotz, Y.; Laval, J.; Laval, F.; Dewhirst, M. W.; Mitchell, J. B. *Carcinogenesis* **1998**, *19*, 711−721

[4] (a) Ford, P. C.; Bourassa, J.; Miranda, K.; Lee, B.; Lorkovic, I.; Boggs, S.; Kudo, S.; Laverman, L. *Coord. Chem. Rev.* **1998**, *171*, 185−202. (b) Bourassa, J.; DeGraff, W.; Kudo, S.; Wink, D. A.; Mitchell, J. B.; Ford, P. C. *J. Am. Chem. Soc.* **1997**, *119*, 2853−2860.

[5] Miranda, K. M.; Bu, X.; Lorkovic, I.; Ford, P. C. *Inorg. Chem.* **1997**, *36*, 4838−4848.

[6] Boggs, S., Ph.D. Dissertation, University of California, Santa Barbara, 1996.

[7] Lorkovic, I. M.; Miranda, K. M.; Lee, B.; Bernhard, S.; Schoonover, J. R.; Ford, P. C. *J. Am. Chem. Soc.* **1998**, *120*, 116474−11683.

[8] (a) Takede, T.; Irie, R.; Shinoda, Y.; Katsuki, T. *Synlett* **1999**, *7*, 1157−1159. (b) Mihara, J.; Hamada, T.; Takede, T.; Irie, R.; Katsuki, T.; *Synlett* **1999**, *7*, 1160−1162. (c) Uchida, T.; Irie, R.; Katsuki, T. *Synlett* **1999**, *7*, 1163−1165.

[9] Odenkirk, W.; Rheingold, A. L.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 6392−6398.

[10] **1** was prepared in accordance with a previously published procedure.[9] The compound was characterized by ^1H NMR, UV−vis, IR, and FAB mass spectrometry.

[11] Leung, W. H.; Che, C. M. *Inorg. Chem.* **1989**, 28, 4619−4622.

[12] Photodissociation of Cl^- would give $[Ru(salen)(sol)(NO)]^+$ with a ν_{NO} band and electronic spectrum analogous to those of **1**. Photodissociation of Cl· would be accompanied by metal center reduction; in contrast the observed LMCT band indicates oxidation to Ru(III). Preliminary studies show that photolysis of the cationic complex $Ru(salen)(H_2O)(NO)^+$ in aqueous solution gives spectral changes analogous to those reported here, again consistent with NO labilization to give $Ru(salen)(H_2O)_2^+$.

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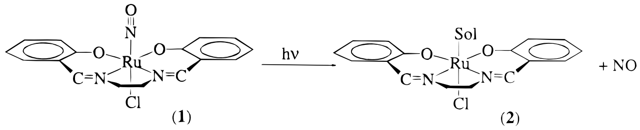
spectral changes[12,13] and both processes are inconsistent with the NO-dependent kinetics for regeneration of **1** described below. Thus, we conclude that the photoreaction is represented by eq 1. The product spectra, especially the LMCT bands, are solvent dependent consistent with the formulation of this species as Ru(salen)(Cl)(Sol) (**2**, Sol = solvent).



(1)

To confirm photodissociation of NO as shown in eq 1, the photolysis of **1** in acetonitrile was carried out in the presence of added Co(TPP) (TPP = tetraphenylporphyrin). Co(TPP) has a Soret band at λ_{max} 412 nm and reacts rapidly with NO to give Co(TPP)(NO) with a λ_{max} at 432 nm. Accordingly, when this solution was irradiated at 365 nm, the Ru(III) photoproduct bands at ~700 nm grew as did the 432 nm absorbance of Co(TPP)(NO).[14]

Quantum yields for eq 1 were determined from spectral changes in aerated acetonitrile to be 0.13 ± 0.01 and 0.09 ± 0.01 for the irradiation wavelengths λ_{irr} = 365 and 436 nm, respectively.[13] The photoreactivity of **1** in other solvents was comparable, but quantitative measurements in some cases were complicated by fast back reactions.

The kinetics for the back reaction (eq 2) were studied by photochemical generation of **2** under excess NO and following the reformation of **1** according to changes in the optical spectra. In donor solvents, the reaction was sufficiently slow to follow using conventional spectrometers; however, in toluene it was necessary to use laser flash photolysis techniques (Figure 2).[13] The transient spectrum recorded 300 ns after 355 nm flash photolysis in that solvent clearly shows formation of **2**. In each solvent, the back reaction kinetics are first order in **2**, and k_{obs} is linearly dependent on [NO] (eq 3).

$$\mathrm{Ru(salen)(Cl)(Sol)} + \mathrm{NO} \xrightarrow{k_{NO}} \mathrm{Ru(salen)(Cl)(NO)} + \mathrm{Sol} \qquad (2)$$

$$\mathrm{d}[\mathbf{1}]/\mathrm{d}t = -\mathrm{d}[\mathbf{2}]/\mathrm{d}t = k_{NO}[\mathrm{NO}][\mathbf{2}] \qquad (3)$$

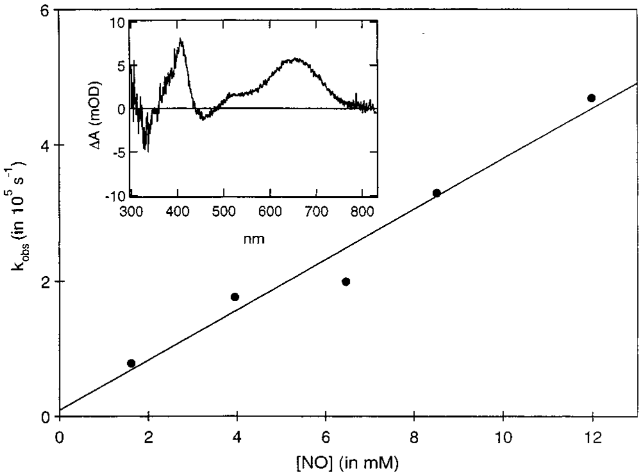


Figure 2. NO concentration dependence of the k_{obs} values for the reaction of **2** with NO in toluene solution at 25 °C after 355 nm flash photolysis of **1** (k_{NO} = 3.7 × 10^7 M^{-1} s^{-1}). Inset: Transient spectrum of **2** recorded 300 ns after the flash using a CCD camera (500 ns gate width) under 649 Torr of NO.

The second-order rate constants obtained from these experiments are as follows: (3.7 ± 0.4) × 10^7 M^{-1} s^{-1} in toluene, 6.4 ± 0.6 M^{-1} s^{-1} in CH_2Cl_2, 0.25 ± 0.05 M^{-1} s^{-1} in THF,[15] and ~5 × 10^{-4} M^{-1} s^{-1} in acetonitrile (25 °C). The NO dependence of the back reaction, the lack of a NO band in the IR, and the formation of a Ru(III) species are consistent with the photoreaction depicted in eq 1. The dramatic variation of rate constants measured in different solvents strongly supports the proposed formation of a solvento species after the loss of NO. These observations also suggest a dissociative or dissociative interchange mechanism for eq 2.

In summary, the ruthenium nitrosyl complex Ru(salen)(Cl)(NO) **1** undergoes NO labilization upon near-UV irradiation to give the solvento species Ru(salen)(Cl)(Sol)**.** Thus, this system has the potential to serve as a precursor for photochemical NO delivery to various targets, although (ongoing) structural modifications to tune spectroscopic and solubility properties are in order. Furthermore, these studies indicate that the Lewis acid, oxene transfer, etc. catalysts formed upon photoactivation of Ru(R-salen)(X)(NO) precursors are the solvento species analogous to **2**. The back reaction to reform **1** from **2** and excess NO varies by 11 orders of magnitude for the solvents probed, and this observation suggests that ligand substitution occurs by a dissociative or dissociative interchange mechanism.

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[13] (a) Flash and continuous photolysis experiments were carried out in solutions deaerated by 3 freeze−pump−thaw cycles except for continuous photolysis experiments in cyclohexane where the oxidation of NO by O_2 from air was used to make that reaction irreversible for spectral analysis. (b) Light intensities for continuous photolysis experiments were determined using ferrioxalate actinometry according to: Calvert, J. G.; Pitts, J. N. *Photochemistry*; J. Wiley and Sons: New York, 1966. (c) Flash experiments used time-resolved optical detection techniques described in ref 7.

[14] Since both Co(TPP) and Co(TPP)NO absorb strongly in the photolysis wavelength regions, this experiment confirms NO formation but only qualitatively. We are currently working on reliable protocols for quantitative determination of very low NO concentrations in nonaqueous media.

[15] (a) The k_{NO} in THF experiment was estimated from the assumption that the solubility of NO in 25 °C THF is approximately that of CO (0.011 mol L^{-1} atm^{-1}).[14b] (b) Payne, M. W.; Leussing, L. L.; Shore, S. G. *J. Am. Chem. Soc.* **1987**, *109*, 617−618.