shows the decomposition mechanism of acetyl benzoyl peroxide.

To our knowledge this is the first infrared detection of the phenyl radical.[8]

In addition, we have also irradiated I with deuterium substitution in the phenyl ring. Photolysis of this species produced the intense 612 cm^{-1} band characteristic of the out of plane bending mode of the methyl radical, the weak 1385, 3150 cm^{-1} bands, and another intense band at 519 cm^{-1} which synchronously disappeared with CH_3 upon warming to 30 K. This intense band at 519 cm^{-1} we assign to the CD out of plane bending mode of the phenyl radical.

Further experimental and theoretical work is being pursued on this system and a more complete account is forthcoming.

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References and Notes

(1) H. C. Box, *J. Phys. Chem.*, **75**, 3426 (1971).

(2) N. J. Karch, E. T. Koh, B. L. Whitsel, and J. M. McBride, *J. Am. Chem Soc.*, in press.

(3) Photolysis was also performed with a filter which transmitted between 3000 and 4000 Å. These conditions did not change any observations.

(4) Species identified by comparison with the matrix ir spectrum of an authentic sample.

(5) Evidence that the integrity of the matrix isolation was maintained during warm up and that the photochemical and thermal reactions occurred within an argon cavity was given by the absence of ethane[4] or diphenyl[4] during the course of the experiments.

(6) A. Snelson, *J. Phys. Chem.*, **74**, 537 (1970).

(7) The possibility of the observed bands stemming from benzoyloxy radicals was excluded on the basis that no carboxyl bands above 1500 cm^{-1} were observed other than those belonging to methyl benzoate. Also warm up experiments did not show an increase in methyl benzoate, the expected combination product of the benzoyloxy-methyl radical pair. In addition, Karch et al.[2] have shown that the benzoyloxy radical is quite photosensitive under similar photolytic conditions to ours. Since their results were obtained using sensitive ESR techniques, we do not expect to see such small concentrations with our relatively insensitive infrared techniques.

(8) For ESR and uv studies on the phenyl radical see P. H. Kasai, E. Hedaya, and E. B. Whipple, *J. Am. Chem. Soc.*, **91**, 4364 (1969); J. E. Bennett, B. Mile, and A. Thomas, *Proc. R. Soc., Ser. A*, **293**, 246 (1966); G. Porter and Ward, *ibid.*, **287**, 457 (1965).

(9) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **47**, 5146 (1967).

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The Influence of Remote Substituents on Redox Potentials in Nitrosoarene Complexes of Ruthenium

Sir:

The effect of coordinated ligands on the properties of a metal center is a fundamental theme of transition metal chemistry.[1-3] Changes in ligands can lead to changes in the electronic structure of complexes and, with widely varying ligands, the properties of the metal center can be strongly affected. A related question, arising from the study of substituent effects in physical organic chemistry[4,5] and still largely unexplored,[6] concerns the sensitivity of the metal center to changes at a remote site on a ligand. We have prepared the series of *para*-nitrosoarene complexes of ruthenium(II), [*cis*-$\mathrm{Ru(bpy)_2}$(*p*-$\mathrm{(N(O)C_6H_4X)Cl}$]$^+$ (bpy is 2,2′-bipyridine; X is $N(CH_3)_2$, $NHCH_3$, OH, Br, H, CH_3, NO_2), and find evidence that even changes in the remote substituent -X can have a profound effect at the metal.

The preparation of the complexes has been described.[7] From spectral studies and the crystal structure of a related palladium complex,[8] it is probable that the ArNO ligands are N-bound. The ruthenium complexes undergo reversible one-electron oxidations and reductions in acetonitrile[9] and have intense absorption bands which can be assigned to dπ → π^* (ArNO) and dπ → π^* (bpy) transitions. The oxidation processes are electrochemically reversible (eq 1).[9] Their potentials fall in a potential range (Table I) common to related bis(2,2′-bipyridine)ruthenium(III)/(II) couples,[10] and the one-electron oxidation products, [$\mathrm{Ru(bpy)_2(N(O)C_6H_4X)Cl}$]$^{2+}$ (X = $N(CH_3)_2$, $NHCH_3$, H, CH_3), prepared by Ce(IV) oxidation have electronic spectral properties in solution expected for Ru(III).[11,12]

Table I. $E_{1/2}$ Values for the Nitrosoarene Complexes [$\mathrm{Ru(bpy)_2}$(*p*-$\mathrm{N(O)C_6H_4X)Cl}$]$^+$ in Acetonitrile[a]

-X	$E_{1/2}$ (OX), V	$E_{1/2}$ (Red), V
$-N(CH_3)_2$	0.77	-0.91
$-NHCH_3$	0.80	-0.90
-OH	0.90	-0.61
$-CH_3$	1.25	-0.71
-H	1.30	-0.69
-Br	1.30	-0.61
$-NO_2$	1.43	-0.39

[a] In 0.1 *M* [$N(n\text{-}C_4H_9)_4$]PF_6–acetonitrile vs. the saturated sodium chloride calomel electrode at 22 + 2° using a Pt bead electrode.

$$[\mathrm{Ru^{III}(bpy)_2(N(O)C_6H_4X)Cl}]^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Ru^{II}(bpy)_2(N(O)C_6H_4X)Cl}]^{+} \quad (1)$$

$$E_{1/2}(\mathrm{OX})$$

The reduction processes are reversible only at relatively fast cyclic voltammetry scan rates, occur in the potential range −0.39 to −0.91 V vs. the SSCE (Table I), and are in the correct potential region to be reductions at bound nitrosoarene (eq 2).[13-15]

$$[\mathrm{Ru^{II}(bpy)_2(N(O)C_6H_4X)Cl}]^{+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [\mathrm{Ru^{II}(bpy)_2(N(O)C_6H_4X\cdot^{-})Cl}] \quad (2)$$

The increase in Ru(III)/(II) reduction potentials as saturated ligands are replaced by π-accepting ligands is well documented and has been attributed to stabilization of the Ru(II) state by π-back-bonding.[3,16] Monotonic increases from 0.1 to 1.25 V[3,17] are observed for Ru(III)/(II) reduction potentials in acidic aqueous solution in couples from $\mathrm{Ru(NH_3)_3}^{3+/2+}$ to $\mathrm{Ru(bpy)_3}^{3+/2+}$ in which NH_3 groups are replaced stepwise by π-back-bonding pyridine ligands. By comparison, the data in Table I are remarkable in that changing the *remote* substituent on the *single* nitrosoarene ligand from $-N(CH_3)_2$ to $-NO_2$ causes an increase in Ru(III)/Ru(II) potential nearly 60% as great (0.77-1.43 V).

The high sensitivity of the filled dπ levels to changes in -X is also reflected in $\bar{\nu}_{\max}$ values for the dπ(Ru(II)) → π^* (bpy) transitions.[18] For these transitions, which involve the 2,2′-bipyridine groups as "spectator" ligands for the Ru-nitrosoarene interaction, $\bar{\nu}_{\max}$ varies directly with $E_{1/2}$(OX) (Table I) in the range 20.7 kK (X = $N(CH_3)_2$) to 24.1 kK (X = NO_2).

The sensitivity of $E_{1/2}$(OX) to -X is shown in the Hammett-type plots in Figures 1 and 2. The correlations between $E_{1/2}$(OX) and the substituent constants σ_R, $\sigma_R{}^0$, and $\sigma_p - \sigma_m$, which have been taken as a measure of pure resonance (π-bonding) effects, are good to excellent.[5,19] The correlation coefficient (*r*) for the data in Figure 1 is 0.970. The correlation with σ_p (Figure 2) is less satisfactory (*r* = 0.937). For the plot in Figure 1, the sensitivity of $E_{1/2}$(OX) to -X is extraordinarily high since the "reaction constant" ρ is 1.05. Much lower reaction constants are observed for redox processes of benzenoid compounds where the substit-

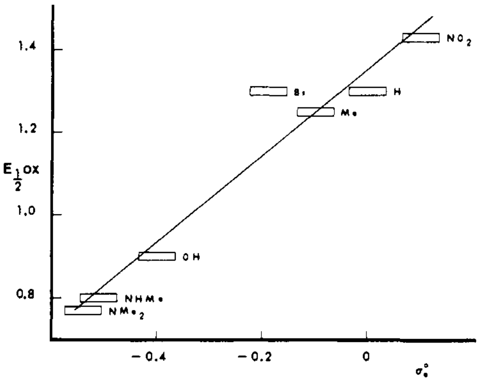

Figure 1. A plot of the Ru(III/II) reduction potentials ($E_{1/2}$OX) vs. $\sigma_R{}^0$. Values of $\sigma_R{}^0$ are taken from ref 6. Error limits are ±0.01 V in $E_{1/2}$(OX) and ±0.03 for $\sigma_R{}^0$ values (ref 23).

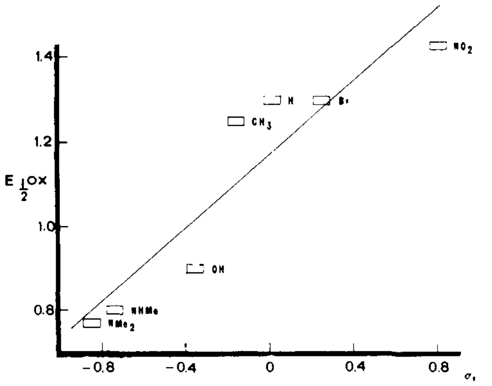

Figure 2. A plot of the Ru(III/II) reduction potentials ($E_{1/2}$OX) vs. σ_p. Values for σ_p are taken from ref 6. Error limits as in Figure 1.

uent groups are directly attached to the aromatic ring.[20]

The Ru(II) nitrosoarene complexes are stable in acetonitrile solution, and, as is the case in metal carbonyl and nitrosyl complexes, the Ru-N(O)Ar linkage may be largely π-bonding in character. This is consistent with the relative instability of first-row transition metal complexes of nitrosoarenes,[21] and the surprising, relatively high lability of some of the Ru(III) nitrosoarene complexes.[22] The chemical evidence and the correlation in Figure 1 are consistent with extensive π-back-bonding from Ru(II), and the effect of -X is probably transmitted mainly through the π-system of the ligand.

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References and Notes

(1) C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, N.Y., 1962.
(2) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, Oxford, 1962.
(3) A. M. Sargeson and D. Buckingham in "Chelating Agents and Metal Chelates", F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N.Y., 1964, Chapter 6.
(4) L. P. Hammett, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N.Y., 1970.
(5) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).
(6) O. Exner in "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Ed., Plenum Press, London, 1972, Chapter 1.
(7) (a) W. L. Bowden, W. F. Little, and T. J. Meyer, *J. Am. Chem. Soc.*, **96**, 5605 (1974); (b) *ibid.*, submitted for publication.
(8) R. G. Little and R. J. Doedens, *Inorg. Chem.*, **12**, 537 (1973).
(9) $E_{1/2}$ values were measured by cyclic voltammetry (50–1000 mV/sec) and stirred solution voltammetry in CH$_3$CN solutions containing 0.1 *M* [N(*n*-butyl)$_4$]NPF$_6$ as supporting electrolyte. A Pt bead electrode was used, and potential values are vs. the saturated sodium chloride calomel electrode (SSCE) at 22 ± 2°. In cyclic voltammetry the ratio of anodic to cathodic peak currents was ~1. Peak separations ($\Delta E_p = E_{p,a} - E_{p,c}$) were nearly independent of sweep rate and slightly higher than the expected 58–59 mV (60–70 mV) because of uncompensated solution resistance. $E_{E1/2}$ values were taken as the average of the peak potentials $E_{p,a}$ and $E_{p,c}$.
(10) G. M. Brown, PhD Thesis, The University of North Carolina, 1974.
(11) G. M. Bryant and J. E. Fergusson, *Aust. J. Chem.*, **24**, 275 (1971).
(12) J. N. Braddock and T. J. Meyer, *J. Am. Chem. Soc.*, **95**, 3158 (1973).
(13) A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852 (1961).
(14) M. Lipsztajn, T. M. Krygowski, E. Laren, and Z. Galus, *J. Electroanal. Chem. Interfacial Electrochem.*, **57**, 339 (1974).
(15) M. R. Asirvatham and M. D. Hawley, *J. Electroanal. Chem. Interfacial Electrochem.*, **57**, 179 (1974).
(16) H. Taube, *Surv. Prog. Chem.*, **6**, 1 (1973).
(17) (a) J. N. Braddock, J. L. Cramer, and T. J. Meyer, *J. Am. Chem. Soc.*, **97**, 1972 (1975), and references therein; (b) J. L. Cramer, Ph.D. Thesis, University of North Carolina, 1975.
(18) G. M. Bryant, J. E. Fergusson, and H. K. J. Powell, *Aust. J. Chem.*, **24**, 257 (1971).
(19) O. Exner in ref 6, Chapter 1.
(20) P. Zuman, *Collect. Czech. Chem. Commun.*, **25**, 3225 (1960).
(21) C. J. Popp and R. O. Ragsdale, *J. Chem. Soc. A*, 1822 (1970); C. J. Popp and R. O. Ragsdale, *Inorg. Chem.*, **7**, 1845 (1968).
(22) W. L. Bowden unpublished results.
(23) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).

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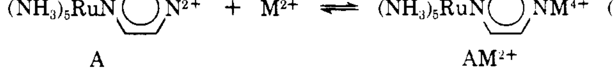
Electron Transfer Photochromism. The Flash Photolysis of the Binuclear Complex (NH$_3$)$_5$Ru^{II}(μ-pyrazine)Cu^{II}

Sir:

Recent studies[1-4] have demonstrated that the metal-to-ligand charge transfer excited states of Ru(bpy)$_3{}^{2+}$ can undergo electron transfer to metal complexes and other oxidants in solution. Observations with several other complexes indicate similar behavior resulting from MLCT excitation.[5,6] Photostimulated electron transfer can be separated into two general classes: in the first, light accelerates a thermodynamically favored reaction (e.g., the photocatalyzed reaction between Ru(bpy)$_3{}^{2+}$ and Tl^{3+})[2] or a reaction giving products which decompose irreversibly (e.g., the proposed reduction of cobalt(III) ammines by excited Ru(bpy)$_3{}^{2+}$).[7] The second category includes those photostimulated electron transfers to produce thermodynamically less favored species which undergo the reverse reaction to regenerate the starting materials.[3,7c] The term *electron transfer photochromism* describes the latter case. Here we report the first demonstration of *intramolecular* electron transfer photochromism between two metal ions of a polynuclear complex.

It was recently reported[8] that the pentaammine(pyrazine)ruthenium(II) complex (A) is a good ligand for several divalent metal ions in aqueous solution (eq 1). The visible



$$\underset{\text{A}}{(NH_3)_5RuN\langle\rangle N^{2+}} + M^{2+} \rightleftharpoons \underset{\text{AM}^{4+}}{(NH_3)_5RuN\langle\rangle NM^{4+}} \quad (1)$$

$(M^{2+} = Cu^{2+}, Zn^{2+}, Ni^{2+})$

spectrum of A is dominated by an intense MLCT absorption band (λ_{max} 472 nm) and association with H$^+$ or M^{2+} shifts this to the red (508 nm for Cu^{2+}, 489 nm for Zn^{2+}, 493 nm for Ni^{2+}, 529 nm for H$^+$).[8,9] Continuous photolysis of A in the MLCT region leads to low photoreaction quantum yields ($\Phi \sim 10^{-3}$). AH$^+$ is an order of magnitude less photoactive.[10,11] Flash photolysis of A or AH$^+$ does not in-