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Oxygen Atom Transfer between *Cis*-Coordinated Nitrite and Nitrosyl Ligands: The Case of the $CpCr(NO)_2(NO_2)$/$CpCr(NO)_2(ONO)$ Linkage Isomers

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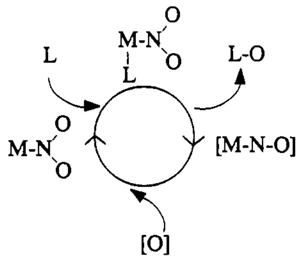
$CpCr(NO)_2(NO_2)$ exists as a mixture of the nitro and nitrito linkage isomers, with the nitrito isomer predominating in both solution and the solid state (Cp = η^5-C_5H_5). The $Cr–NO_2 \rightleftarrows Cr–ONO$ equilibrium is markedly solvent and temperature dependent: in $CDCl_3$, ΔH_{eq} = 1.8(3) kcal/mol and ΔS_{eq} = 9.3(9) eu. The treatment of $CpCr(NO)_2(NO_2)$ with $Na^{15}NO_2$ in MeOH leads to the exchange of free and bound NO_2^-, eventually giving a statistical distribution of the ^{15}N label in the NO and NO_2 ligands and free NO_2^- at equilibrium. The linkage isomers of the labeled $CpCr(NO)_2(^{15}NO_2)$ complex convert to a statistical mixture of the $CpCr(^{15}NO)(NO)(NO_2)$ and $CpCr(^{15}NO)(NO)(ONO)$ isotopomers in solution and in the solid state. The initial disappearance rate of the $CpCr(NO)_2(^{15}NO_2)$ isotopomer is first-order, leading to ΔH^* = 11.3(6) kcal/mol and ΔS^* = 10(2) eu in MeOH and ΔH^* = 14(1) kcal/mol and ΔS^* = 20(1) eu in toluene. This behavior, together with the fact that $CpCr(NO)_2(^{15}NO_2)$ equilibrates to $CpCr(^{15}NO)(NO)(NO_2)$ in the solid state, supports an intramolecular O atom transfer process between *cis*-coordinated NO and NO_2 ligands.

Introduction

Studies of nitrite coordination to transition metals provided some of the first examples of linkage isomerism and led to early discussions on the role of hydroxyl and oxo group transfer from metal centers to substrates like N_2O_3.[2,3] More recently, transition metal complexes containing the NO_2 ligand were extensively studied as catalysts for the mild oxidation of simple organic substrates.[4] A notable feature of metal–nitro oxidation catalysts is the regeneration of the active nitro species by oxidation of the metal–nitrosyl intermediate that remains after O atom transfer to the substrate, (Scheme I).[5]

Reversible intramolecular O atom transfer between *cis*-$(NO_2)(NO)$ groups of *cis*-$[Fe(NO)(NO_2)(S_2CN(Me)_2)_2]$ was first reported by Feltham and Ileperuma.[6] The conversion of *cis*-$Pt(NO)(NO_3)(PPh_3)_2$ to *cis*-$Pt(NO_2)_2(PPh_3)_2$ is believed to occur by an irreversible O atom transfer between *cis*-coordinated NO and NO_3 ligands.[7] Numerous investigations have addressed intramolecular O atom transfer from a NO_2 ligand to an adjacent CO ligand, leading to spontaneous CO_2 loss and the formation of nitrosyl complexes.[8] Cooper and co-workers have demonstrated a similar CO/CO_2 oxygen atom transfer process when $[W(CO)_5]^{2-}$ is treated with carbon dioxide.[9]

Scheme I



Reported herein is an examination of nitro/nitrosyl interconversion in the $CpCr(NO)_2(NO_2)$ system. In analogy to Feltham and co-workers,[6] who discovered the *cis*-nitro(nitrosyl) O atom exchange process, we were intrigued by the possibility of an intramolecular "round-about" O atom transfer process about the *fac*-coordination sites of a three-legged piano stool complex. The study first addresses the issue of nitro/nitrito linkage isomer equilibrium for $CpCr(NO)_2(NO_2)$. Through the use of ^{15}N-labeling experiments, we show the equilibration of the ^{15}N label into the nitrosyl ligands. A kinetic assessment of the intramolecular O atom transfer process over a 50 °C temperature range leads to the first determination of activation parameters for a NO/NO_2 oxygen atom transfer process.

Results

Characterization of $CpCr(NO)_2(NO_2)$. $CpCr(NO)_2(NO_2)$ is most efficiently prepared from the metathesis of $CpCr(NO)_2Cl$ with $NaNO_2$ in MeOH. Oxidation of $CpCr(NO)_2(NO_2)$ in air gives $CpCr(NO)_2(NO_3)$ with attendant decomposition. Spectral

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(1) (a) Utah State University. (b) University of Vermont.

(2) (a) Basolo, F.; Hammaker, G. S. *Inorg. Chem.* **1962,** *1,* 1. (b) Jorgensen, S. M. *Z. Anorg. Allg. Chem.* **1894,** *5,* 169.

(3) (a) Holm, R. H. *Chem. Rev.* **1987,** *87,* 1401. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988. (c) Herrmann, W. A.; Jung, K. A.; Schafer, A.; Kneuper, H. *Angew. Chem., Int. Ed. Engl.* **1987,** *26,* 464.

(4) (a) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981. (b) Solar, J. P.; Mares, F.; Diamond, S. E. *Catal. Rev.—Sci. Eng.* **1985,** *27,* 1. (c) Tovrog, B. S.; Diamond, S. E.; Mares, F. *J. Am. Chem. Soc.* **1979,** *101,* 270. (d) Andrews, M. A.; Kelly, K. P. *J. Am. Chem. Soc.* **1981,** *103,* 2894. (e) Andrews, M. A.; Cheng, C. W. F. *J. Am. Chem. Soc.* **1982,** *104,* 4268. (f) Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F.; Emge, T. J.; Kelly, K. P.; Koetzle, T. F. *J. Am. Chem. Soc.* **1984,** *106,* 5913. (g) Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F.; Kelly, K. P. *Organometallics* **1984,** *3,* 1777. (h) Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F. *Organometallics* **1985,** *4,* 268. (i) Backvall, J. E.; Heumann, A. *J. Am. Chem. Soc.* **1986,** *108,* 7107.

(5) (a) Leising, R. A.; Takeuchi, K. J. *J. Am. Chem. Soc.* **1988,** *110,* 4079. (b) Muccigrosso, D. A.; Mares, F.; Diamond, S. E.; Solar, J. P. *Inorg. Chem.* **1983,** *22,* 960. (c) Mares, F.; Diamond, S. E.; Regina, F. J.; Solar, J. P. *J. Am. Chem. Soc.* **1985,** *107,* 3545.

(6) (a) Ileperuma, O. A.; Feltham, R. D. *J. Am. Chem. Soc.* **1976,** *98,* 6039. (b) Ileperuma, O. A.; Feltham, R. D. *Inorg. Chem.* **1977,** *16,* 1876.

(7) Bhaduri, S. A.; Bratt, I.; Johnson, B. F. G.; Khair, A.; Segal, J. A.; Walters, R.; Zuccaro, C. *J. Chem. Soc., Dalton Trans.* **1981,** 235.

(8) (a) Booth, G.; Chatt, J. *J. Chem. Soc.* **1962,** 2099. (b) Doughty, D. T.; Gordon, G.; Stewart, R. P. *J. Am. Chem. Soc.* **1979,** *101,* 2645. (c) Feltham, R. D.; Kriege, J. C. *J. Am. Chem. Soc.* **1979,** *101,* 5064. (d) Kriege-Simondsen, J.; Elbaze, G.; Dartinguenave, M.; Feltham, R. D.; Dartinguenave, Y. *Inorg. Chem.* **1982,** *21,* 230. (e) Kriege-Simondsen, J. C.; Bailey, T. D.; Feltham, R. D. *Inorg. Chem.* **1983,** *22,* 3318. (f) Kriege-Simondsen, J.; Feltham, R. D. *Inorg. Chim. Acta* **1983,** *71,* 185. (g) Baker, P. K.; Broadley, K.; Connelly, N. G. *J. Chem. Soc., Chem. Commun.* **1980,** 775. (h) Baker, P. K.; Broadley, K.; Connelly, N. G. *J. Chem. Soc., Dalton Trans.* **1982,** 471. (i) Stevens, R. E.; Gladfelter, W. L. *Inorg. Chem.* **1983,** *22,* 2034. (j) Mantell, D. R.; Gladfelter, W. L. *J. Organomet. Chem.* **1988,** *347,* 333. (k) Doughty, D. T.; Stewart, R. P.; Gordon, G. *J. Am. Chem.* **1981,** *103,* 3388. (l) Gordon, C. M.; Feltham, R. D.; Turner, J. J. *J. Phys. Chem.* **1991,** *95,* 2889.

(9) Maher, J. M.; Lee, G. R.; Cooper, N. J. *J. Am. Chem. Soc.* **1982,** *104,* 6797.

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Table I. ^1H NMR (η^5-C_5H_5) Chemical Shift Values (ppm) and Nitro/Nitrito Equilibrium Constants for $CpCr(NO)_2(NO_2)$ at 20 °C in Various NMR Solvents

	δ(Cp)			
solvent	nitro isomer	nitrito isomer	$\Delta\delta$	K_{eq} $Cr(NO_2) \leftrightarrow Cr(ONO)$
acetone-d_6	6.01	5.92	0.09	8.7
toluene-d_8	4.60	4.56	0.04	13.9
CD_2Cl_2	5.80	5.70	0.10	4.9
dmso-d_6	6.06	5.99	0.07	4.1
CD_3CN	5.85	5.77	0.08	4.3
$CDCl_3$	5.79	5.66	0.13	4.7
C_6D_6	4.54	4.50	0.04	11.4
CD_3OD	5.95	5.83	0.12	4.0
$CDCl_3/C_6D_6$ (0.5/0.5 v/v)	4.98	4.94		6.0

characterization of pure $CpCr(NO)_2(NO_2)$ by ^1H and ^{13}C NMR and IR spectroscopies indicates the presence of an equilibrium mixture of linkage isomers in solution. X-ray diffraction analysis of single-crystal samples of $CpCr(NO)_2(NO_2)$ confirms the presence of the nitrito isomer.[10] Powder X-ray diffraction results for finely-ground samples of bulk $CpCr(NO)_2(NO_2)$ show the presence of a minor crystalline phase in addition to the major peaks predicted for the nitrito isomer. The thermodynamic parameters for the isomer equilibrium are determined by variable-temperature ^1H NMR experiments. Interpretation of these data is presented in the Discussion.

^{15}N-Labeling Experiments. Treatment of $CpCr(NO)_2Cl$ with a slight excess of $Ag^{15}NO_2$ in a water/acetone slurry gives $CpCr(NO)_2(^{15}NO_2)$ in good yield. Data from ^{15}N NMR spectroscopy show that the nitro and nitrito ligands are quickly exchanged with free ($^{15}NO_2^-$) when $CpCr(NO)_2(NO_2)$ is treated with $Na^{15}NO_2$ in MeOH. Subsequent IR and ^{15}N NMR data show the statistical distribution of the ^{15}N label in all N sites when the system reaches equilibrium. Assessment of the initial rate of ^{15}N equilibration starting from the $CpCr(NO)_2(^{15}NO_2)$ isotopomer by quantitative IR spectroscopy between 0 and 50 °C permits the determination of the activation parameters for the reaction and a mechanistic discussion of the O atom transfer between NO and NO_2 ligands.

Discussion

Formation and Characterization of Linkage Isomers of $CpCr(NO)_2(NO_2)$. Although there are numerous reports of the preparation of $CpCr(NO)_2(NO_2)$,[10,11] the complex is most efficiently synthesized by metathesis of $CpCr(NO)_2Cl$ with excess nitrite in MeOH (eq 1).

$$CpCr(NO)_2Cl + NaNO_2 \xrightarrow{MeOH} CpCr(NO)_2(NO_2) + NaCl \tag{1}$$

Using ^1H NMR spectroscopy to monitor the reaction of a CD_3OD solution of $CpCr(NO)_2Cl$ with 1 equiv of $NaNO_2$, we observe the development of two new signals at δ 5.83 and 5.95 in a ca. 4:1 ratio. After 1 h, the signal from $CpCr(NO)_2Cl$ is less than 10% of its original intensity.

The ^1H NMR data for pure $CpCr(NO)_2(NO_2)$ in a variety of solvents are presented in Table I. Two signals attributed to the Cp ligand are consistently present in relative intensities that are purely solvent dependent. Such behavior strongly suggests the presence of an equilibrium of nitro and nitrito linkage isomers for $CpCr(NO)_2(NO_2)$ (eq 2). The effect of solvent on the relative population of linkage isomers is well-known.[12] Previous characterizations of $CpCr(NO)_2(NO_2)$ using low-field ^1H NMR instrumentation were apparently unable to detect the linkage isomers due to the small difference in their chemical shifts. The ^{13}C NMR spectrum for $CpCr(NO)_2(NO_2)$ in $CDCl_3$ also suggests the presence of linkage isomers. Two signals appearing in the region characteristic for skeletal carbon atoms of the Cp ligand have relative intensities matching those observed in the ^1H NMR spectrum.

$$CpCr(NO)_2(NO_2) \rightleftarrows CpCr(NO)_2(ONO) \tag{2}$$

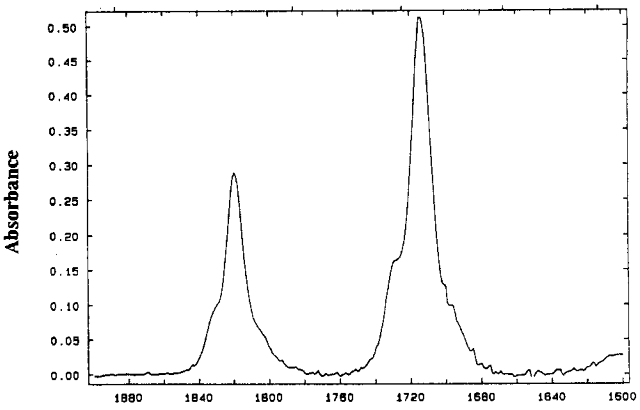

Figure 1. IR spectrum of $CpCr(NO)_2(NO_2)$ in CH_2Cl_2.

Assignment of the linkage isomers in the ^1H NMR spectra is possible with the aid of IR spectroscopy. The IR spectrum of $CpCr(NO)_2(NO_2)$ in CH_2Cl_2 (Figure 1) shows major symmetric and asymmetric nitrosyl ν_{NO} absorptions of $CpCr(NO)_2(NO_2)$ at 1819 and 1714 cm^{-1}, with high-energy shoulders appearing at 1833 and 1728 cm^{-1} (Figure 1). Quantitative analysis of the IR spectrum indicates a 1:5 mixture of isomers, in good agreement with the ^1H NMR data. On the basis of the assumption that the nitro ligand is the stronger π-acceptor and the nitrito ligand is the stronger σ- and π-donor, the major ν_{NO} absorptions are assigned as the O-bound nitrito isomer and the high-energy shoulders are assigned as the N-bound nitro isomer. Accordingly, the more intense ^1H NMR resonance for $CpCr(NO)_2(NO_2)$ is assigned as the O-bound nitrito isomer. The upfield position of the Cp resonance of the nitrito isomer (relative to the nitro isomer) would appear to be a manifestation of a more shielded Cp proton environment. The fingerprint region of the IR spectrum of $CpCr(NO)_2(NO_2)$ is also consistent with the presence of a major nitrito isomer (1425 and 1048 cm^{-1}) and a minor nitro isomer (1385 and 1325 cm^{-1}).[13]

Variable-temperature ^1H NMR data for the isomer equilibrium in $CDCl_3$ permits a van't Hoff analysis (Table II, Figure 2). The nitrito isomer is slightly favored at high temperature, with ΔH = 1.8(3) kcal/mol and ΔS = 9.3(9) eu. Consistent with earlier studies of NO_2 linkage isomerism, the positive entropy term is attributed to a greater entropy for the nitrito isomer.[14] The line shapes of the two ^1H NMR signals do not change over this temperature range, showing isomer exchange to be slow on the NMR time scale.

A complete single-crystal X-ray diffraction analysis of $CpCr(NO)_2(NO_2)$ from our laboratory is in good agreement with

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(10) X-ray data for $CpCr(NO)_2(NO_2)$ (this work) ($C_5H_5N_3O_4Cr$, MW 223.1): orthorhombic space group $Pna2_1$, $a = 13.285(1)$ Å, $b = 6.4539(4)$ Å, $c = 9.829(3)$ Å, $V = 842.7(3)$ Å^3, $Z = 4$, $R/R_w = 5.60/6.80$. Also see: Eremenko, I. L.; Pasynskii, A. A.; Kalinnikov, V. T.; Struchkov, Y. T.; Aleksandrov, G. G. *Inorg. Chim. Acta* **1981**, *52*, 107.

(11) (a) Wilkinson, G.; Piper, T. S. *J. Inorg. Nucl. Chem.* **1956**, *2*, 38. (b) Legzdins, P.; Hames, B. W.; Martin, D. T. *Inorg. Chem.* **1978**, *17*, 3644.

(12) (a) Pavaiglianiti, A. J.; Fultz, W. C.; Burmeister, J. L. *Synth. React. Inorg. Met. Chem.* **1989**, *19*, 469 and references therein. (b) Our data show that low solvent polarity generally favors larger K_{eq} and results in a smaller $\Delta\delta$ value for the Cp ligands in the ^1H NMR spectrum.

(13) (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley and Sons: New York, 1986; pp 221–227. (b) Hitchman, M. A.; Rowbottom, G. L. *Coord. Chem. Rev.* **1982**, *42*, 55.

(14) Ferraro, J. R.; Fabbrizzi, L. *Inorg. Chim. Acta* **1978**, *26*, L15.

Table II. Nitro/Nitrito Equilibrium Constants at Various Temperatures in $CDCl_3$

temp (°C)	K_{eq} $Cr(NO_2) \leftrightarrow Cr(ONO)$	temp (°C)	K_{eq} $Cr(NO_2) \leftrightarrow Cr(ONO)$
40	6.6	0	3.6
30	4.8	−10	3.5
22	4.6	−20	3.0

the crystal and molecular structure reported by Eremenko et al.[10] The complex possesses a piano stool geometry, with a nearly planar Cr–O–N–O linkage (0.1-Å deviation) lying ca. 11° out of the mirror plane of the $[CpCr(NO)_2]$ moiety. The major peaks observed in the powder X-ray diffraction spectrum for a finely-ground sample of analytically pure $CpCr(NO)_2(NO_2)$ agree well with the peaks calculated from our single-crystal data on the nitrito isomer. Additional peaks in the powder diffraction spectrum show the presence of a minor crystalline component that is likely due to the nitro isomer of $CpCr(NO)_2(NO_2)$.

Reactivity of $CpCr(NO)_2(NO_2)$. Solutions of $CpCr(NO)_2(NO_2)$ in CH_2Cl_2, $CDCl_3$, and acetone oxidize in the air to give $CpCr(NO)_2(NO_3)$ (eq 3). The nitrato complex exhibits a single

$$\mathrm{CpCr(NO)_2(NO_2)} + \mathrm{O_2} \rightarrow \mathrm{CpCr(NO)_2(NO_3)} \qquad (3)$$

^1H NMR resonance at δ 5.75 in $CDCl_3$, falling midway between the signals of the nitro and nitrito isomers of $CpCr(NO)_2(NO_2)$.[15] The close proximity of these NMR signals and their corresponding ν_{NO} absorptions in the IR spectrum has led to some confusion between these complexes in the past.[16] For example, we have found that previous routes to $CpCr(NO)_2(NO_2)$ via the treatment of $[CpCr(NO)(\mu\text{-}NO)]_2$ or CpCr(CO)(NO)THF with NO are complicated by the formation of the nitrato complex $CpCr(NO)_2(NO_3)$.[11b] A final complicating factor is the slow (aerobic) decomposition of $CDCl_3$ solutions of both $CpCr(NO)_2(NO_2)$ and $CpCr(NO)_2(NO_3)$ to $CpCr(NO)_2Cl$ (eqs 4 and 5).

$$\mathrm{CpCr(NO)_2(NO_2)} \xrightarrow{\mathrm{CDCl_3/O_2}} \mathrm{CpCr(NO)_2Cl} \qquad (4)$$

$$\mathrm{CpCr(NO)_2(NO_3)} \xrightarrow{\mathrm{CDCl_3/O_2}} \mathrm{CpCr(NO)_2Cl} \qquad (5)$$

Figure 3 shows that the exchange of bound and free NO_2^- can be detected by ^{15}N NMR spectroscopy when $CpCr(NO)_2(NO_2)$ is treated with excess $Na^{15}NO_2$ in CD_3OD (Figure 3). Within 2 h of mixing, NO_2 metathesis leads to the appearance of a major ^{15}N signal at δ 222 and a minor signal at δ 118. From comparison to previous ^{15}H NMR studies, the low-field signal is assigned to the O-bound nitrito ligand and the upfield signal to the N-bound nitro ligand.[17] After 24 h, two additional signals are clearly visible at δ 181 and 163. From the similarity to the NMR data for other $CpM(NO)_2$–metal complexes,[18] we assign these new absorptions to NO ligands which have become enriched with ^{15}N. The intensity of the signal at δ 181 (compared to the δ 163 signal) is consistent with its assignment to the NO ligand in the major nitrito isomer.

The incorporation of the ^{15}N label of free $^{15}NO_2^-$ into the nitrosyl ligands is easily observed by IR spectroscopy. Figure 4 shows the nitrosyl absorptions observed when $CpCr(NO)_2(NO_2)$ is treated with 5 equiv of $Na^{15}NO_2$ in MeOH for 5 d. The symmetric and asymmetric nitrosyl absorptions are each split into three major bands. The nitrosyl ν_{NO} absorptions at highest energy (1817, 1713 cm^{-1}) are from the $[Cr(^{14}NO)_2]$ functional group and those at lowest energy (1784, 1684 cm^{-1}) are assigned to the $[Cr(^{15}NO)_2]$ functional group. The absorptions of the $[Cr(^{14}NO)(^{15}NO)]$ functional group fall midway at 1804 and 1695 cm^{-1}. Table III shows the observed equilibrium isotopomer populations to be nearly statistical when 1 and 5 equiv of $Na^{15}NO_2$ are added to $CpCr(NO)_2(NO_2)$ in MeOH. Thus, the degree of ^{14}N or ^{15}N incorporation simply mirrors the NO/NO_2 isotopic abundance of the solution.

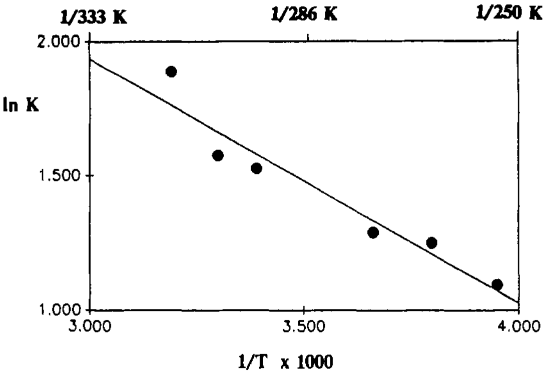

Figure 2. van't Hoff plot for the nitro/nitrito equilibrium.

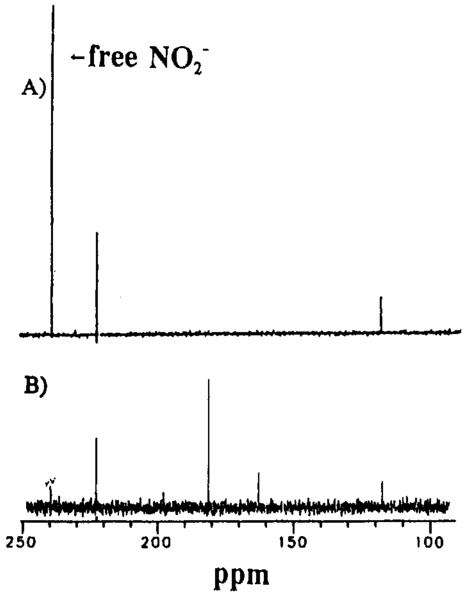

Figure 3. (A) ^{15}N NMR spectrum of a 5:1 mixture of $Na^{15}NO_2$ and $CpCr(NO)_2(NO_2)$ in CD_3OD 2 h after mixing. (B) ^{15}N NMR spectrum of the same solution after 24 h.

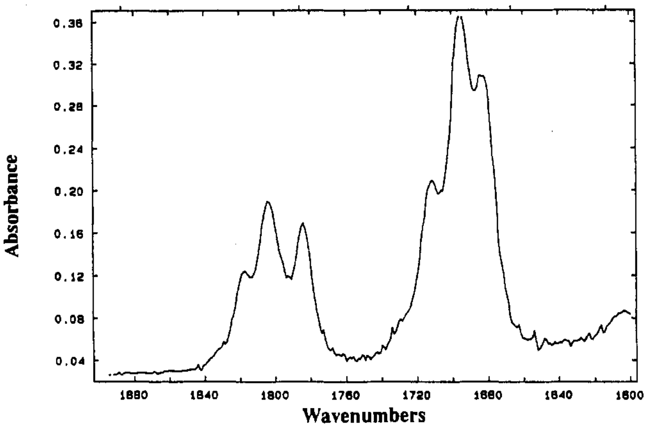

Figure 4. IR spectrum (CH_2Cl_2) of a 5:1 solution of $Na^{15}NO_2$ and $CpCr(NO)_2(NO_2)$ 5 d after mixing.

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[15] This was confirmed by comparison to an authentic sample: Regina, F. J.; Wojcicki, A. *Inorg. Chem.* **1980**, *19*, 3803.

[16] Heating pure $CpCr(NO)_2(NO_2)$ to 100 °C in a vacuum cell results in the observation of NO_2 by gas-phase IR spectroscopy (no NO). Since decomposition to NO was detected in the photoelectron study of $CpCr(NO)_2(NO_2)$ (Legzdins, P.; Chen, H. W.; Jolly, W. J.; Xiang, S. F. *Inorg. Chem.* **1981**, *20*, 1779), the sample was most likely $CpCr(NO)_2(NO_3)$.

[17] Vallenilla, C. D. Ph.D. Thesis, The University of Arizona, 1985.

[18] Botto, R. E.; Kolthammer, B. W. S.; Legzdins, P.; Roberts, J. D. *Inorg. Chem.* **1979**, *18*, 2049.

Table III. Isotopomer Populations in the Reaction of $CpCr(NO)_2(NO_2)$ + $Na^{15}NO_2$ in MeOH at 24 °C

(a) 1 equiv of $Na^{15}NO_2$

time (d)	% [$Cr(^{14}NO)_2$]	% [$Cr(^{14}NO)(^{15}NO)$]	% [$Cr(^{15}NO)_2$]
0	100	0	0
1	72	20	8
2	66	28	6
3	60	31	9
4	59	33	8
5	57	36	7
equilibrium (calcd)	56	38	6

(b) 5 equiv of $Na^{15}NO_2$

time (d)	% $(^{14}NO)_2$	% $(^{14}NO)(^{15}NO)$	% $(^{15}NO)_2$
0	100	0	0
1	26	46	28
2	19	44	37
3	16	43	41
4	17	43	40
5	16	43	41
equilibrium (calcd)	14	47	39

Table IV. Initial Rate of $CpCr(NO)_2(^{15}NO_2)$ Disappearance at Various Concentrations of Complex (24 °C)

$CpCr(NO)_2(^{15}NO_2)$ concn (M × 10^3)	obsd rate (M s^{-1} × 10^9)	$CpCr(NO)_2(^{15}NO_2)$ concn (M × 10^3)	obsd rate (M s^{-1} × 10^9)
1.00	5.89	4.46	1.79
2.01	3.46	8.92	0.78
3.07	2.41		

Mechanism of ^{15}N Scrambling. At 50 °C crystalline $CpCr(NO)_2(^{15}NO_2)$ equilibrates to $CpCr(^{15}NO)(NO)(NO_2)$. The fact that no corresponding increase in the amount of $CpCr(^{15}NO)_2(NO_2)$ occurs suggests the operation of an intramolecular O atom transfer process in this system.

The data for initial disappearance of the $CpCr(NO)_2(^{15}NO_2)$ isotopomer in MeOH at 24 °C are presented in Table IV, and the process is shown in Figure 5 to be first-order in complex.

Kinetic data for the initial disappearance of $CpCr(NO)_2(^{15}NO_2)$ under a variety of temperature and solvent conditions are presented in Table V; the data for the reaction in MeOH are plotted in Figure 6.

The Eyring analysis for the scrambling process in MeOH, shown in Figure 7, gives activation parameters $\Delta H^* = 11.3(6)$ kcal/mol and $\Delta S^* = 10(3)$ eu. In toluene the activation parameters are $\Delta H^* = 14(3)$ kcal/mol and $S^* = 20(1)$ eu. Thus, within the error limits of our kinetic measurements, there is no significant difference in the rates of ^{15}N label scrambling in $CpCr(NO)_2(^{15}NO_2)$ in MeOH and toluene. Since dissociation of the NO_2^- ligand is expected to be suppressed in a nonpolar solvent like toluene, this evidence supports an intramolecular O atom transfer process that does not involve dissociation of the NO_2 ligand. In a control reaction, we found that no detectable ^{15}N label appears in the NO ligands of $CpCr(NO)_2(CH_3)$ after 4 d when the complex is treated with a slight excess of $Na^{15}NO_2$ in MeOH (eq 6).

$$CpCr(NO)_2(CH_3) + Na^{15}NO_2 \rightarrow \text{no reaction} \qquad (6)$$

The existence a nitro/nitrito isomer equilibrium for $CpCr(NO)_2(NO_2)$ prevents the unambiguous determination of which isomer is involved in the O atom transfer. In fact, it is possible that both processes shown in Scheme II are operative.[19,20] The positive entropy term from the Eyring analysis would be more consistent with a five-membered ring for a nitrito transition state compared to a more symmetric (C_s) four-membered ring for a nitro transition state. Matrix isolation studies for the photoinitiated O atom transfer in $CpRu(CO)_2(NO_2)$ have recently made a strong case for the O atom transfer to a *cis*-CO ligand via the nitrito isomer.[81]

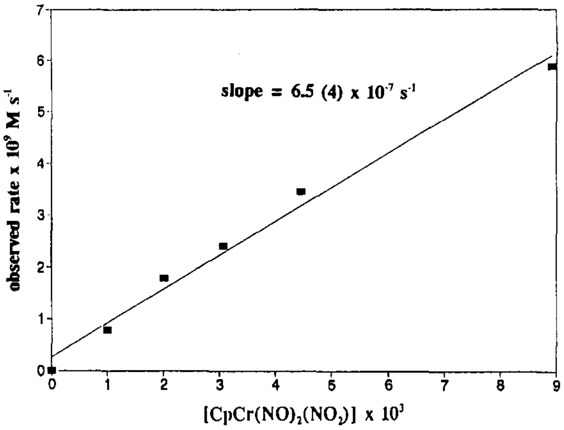

Figure 5. First-order plot for the disappearance of $CpCr(NO)_2(^{15}NO_2)$ at 24 °C.

Table V. Initial Rate Data for the Disappearance of the $CpCr(NO)_2(^{15}NO_2)$ Isotopomer

reacn medium	temp (°C)	k (s^{-1})	time monitored (d)
solid	50	4.3(8) × 10^{-7}	3.0
MeOH	0	1.5(1) × 10^{-7}	5.0
MeOH	24	7.8(5) × 10^{-7}	4.0
MeOH	35	1.3(1) × 10^{-6}	2.0
MeOH	50	4.0(2) × 10^{-6}	1.0
toluene	23	4(1) × 10^{-7}	5.0
toluene	36	1.3(1) × 10^{-6}	2.0
toluene	44	2.0(2) × 10^{-6}	2.0

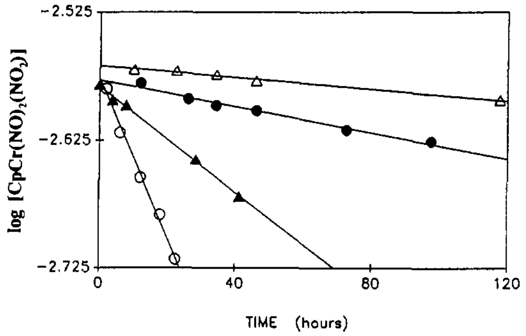

Figure 6. Temperature dependence of the rate of disappearance of $CpCr(NO)_2(^{15}NO_2)$: △, 0 °C; ●, 24 °C; ▲, 35 °C; ○, 50 °C.

Regardless of which isomer is actually involved in the transfer of an oxygen to a *cis*-nitrosyl ligand, we have been able to show that the activation barrier for the NO/NO_2 oxygen atom process is quite low for this first-row nitrosyl complex. Studies currently underway in our laboratory are addressing O atom transfer processes for other related systems.

Experimental Section

All reactions were carried out using standard Schlenk techniques. The nitrogen reaction atmosphere was purified by passing through scavengers for water (Aquasorb, Mallinkrodt) and oxygen (Catalyst R3-11, Chemical Dynamics, So. Plainfield, NJ). Reagent grade solvents were dried over appropriate drying agents and saturated with N_2 prior

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(19) (a) Beck, I. E.; Gusevskaya, E. V.; Stepanov, A. G.; Likholobov, V. A.; Nekipelov, V. M.; Yermakov, Y. I.; Zameraev, K. I. *J. Mol. Catal.* **1989**, *50*, 167. (b) Gusevskaya, E. V.; Beck, I. E.; Stepanov, A. G.; Likholobov, V. A.; Nekipelov, V. M.; Yermakov, Y. I.; Zameraev, K. I. *J. Mol. Catal.* **1986**, *37*, 177.

(20) Connor, J. A.; Riley, P. I. *J. Chem. Soc., Dalton Trans.* **1979**, 1231.

(21) Legzdins, P.; Hoyano, J. K.; Malito, J. T. *Inorg. Synth.* **1978**, *18*, 126.

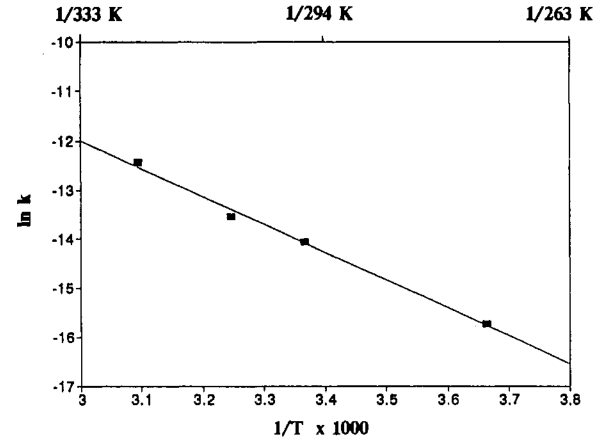
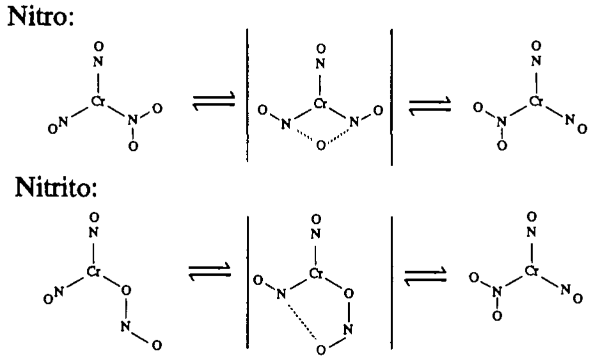


Figure 7. Erying plot for the disappearance of CpCr(NO)$_2$(^{15}NO$_2$).

Scheme II



to use. CpCr(NO)$_2$Cl was prepared by literature methods.[21] Na^{15}NO$_2$ and Na^{15}NO$_2$ (99% isotopic purity) were obtained from Isotec. Routine filtrations were performed through Analytical Filter Pulp (Schliesser and Schull). Infrared spectra were recorded on solutions (0.1-mm NaCl cells) at 2.0-cm^{-1} resolution with a Mattson Polaris-Icon FT spectrophotometer. NMR spectra (^{1}H, ^{13}C, ^{15}N) were recorded on a Varian XL-300 spectrometer operating at 300, 75.4, and 30.4 MHz, respectively. The following residual solvent peaks were used as internal references in the ^{1}H NMR spectra: acetone-d_6, δ 2.04; toluene-d_8, δ 2.09; CD$_2$Cl$_2$, δ 5.32; dmso-d_6, δ 2.49; CD$_3$CN, δ 1.93; CDCl$_3$, δ 7.24 (δ 77.0 for ^{13}C); C$_6$D$_6$, δ 7.15; CD$_3$OD, δ 3.30. ^{15}N NMR spectra were referenced to an external standard of 0.30 M Na^{15}NO$_3$ prepared in D$_2$O. (The chemical shift of this solution relative to neat nitromethane (δ 0.0) has been determined to be δ 3.53.[22]) ^{15}N data collection parameters: acquisition time = 3.00 s; relaxation delay = 5 s between pulses; pulse widths = 10 μs (36°); proton decoupling on; T = 22 °C. X-ray powder diffraction data were collected on a Siemens Krystalloflex IV spectrometer using Ni-filtered Cu Kα radiation (λ = 1.5418 Å), operating at 30 kV and 16 mA; data analysis was performed using the Theta·XRD software (Dapple Systems). No decomposition of the solid CpCr(NO)$_2$NO$_2$ to CpCr(NO)$_2$NO$_3$ was detected during the 10-min data collection. Single-crystal X-ray crystal diffraction analysis was performed on a Siemens P4 autodiffractometer utilizing SHELXTL PLUS software for structure solution and refinement. Powder X-ray diffraction data for single-crystalline CpCr(NO)$_2$(NO$_2$) were calculated using the SHELXTL PLUS routine XPOW. The calculated and observed powder X-ray data are available as supplementary material. Combustion analysis was performed by Atlantic Microlab, Inc., Norcross, GA.

Preparation of CpCr(NO)$_2$(NO$_2$). A Schlenk tube was charged with CpCr(NO)$_2$Cl (0.42 g, 2.0 mmol), 60 mL of N$_2$-saturated methanol, NaNO$_2$ (1.5 g, 22 mmol), and a stir bar. After the mixture was stirred overnight, the methanol was removed in vacuo and the residue extracted with CH$_2$Cl$_2$ (3 × 100 mL). Filtration to remove the NaCl and excess NaNO$_2$, followed by solvent removal and recrystallization at –40 °C from hexane/CH$_2$Cl$_2$, afforded 0.35 g of CpCr(NO)$_2$(NO$_2$) (1.6 mmol, 80%) as olive green crystals. ^{1}H NMR (CDCl$_3$): δ 5.79 (Cp of nitro isomer), 5.66 (Cp of nitrito isomer). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 102.57 (Cp of nitro isomer), 102.24 (Cp of nitrito isomer). IR (CH$_2$Cl$_2$, cm^{-1}): ν_{NO} 1833 (sh), 1819 (vs), 1728 (sh), 1714 (vs). IR (KBr, cm^{-1}): δ_{NO_2} 1385 (s), 1325 (s) (nitro), 1425 (s), 1048 (s) (nitrito). Anal. Calcd for C$_5$H$_5$N$_3$O$_4$Cr: C, 26.91; H, 2.26; N, 18.84. Found: C, 27.11; H, 2.23; N, 18.73. Mp: 80–83 °C.

Preparation of CpCr(NO)$_2$(^{15}NO$_2$). To a Schlenk tube containing AgNO$_3$ (0.161 g, 0.948 mmol) dissolved in 5 mL of H$_2$O was added a solution of Na^{15}NO$_2$ (0.066 g, 0.943 mmol) in 5 mL of H$_2$O. A solution containing CpCr(NO)$_2$Cl (0.100 g, 0.470 mmol) in 25 mL of acetone was added to the milky suspension of Ag^{15}NO$_2$, and the mixture was stirred vigorously for 30 min. The reaction mixture was filtered, and the acetone was removed in vacuo. The remaining aqueous fraction was extracted twice with 20-mL portions of CH$_2$Cl$_2$ and briefly dried over anhydrous MgSO$_4$. The CH$_2$Cl$_2$ extracts were filtered and taken to dryness in vacuo, affording 0.080 g (0.36 mmol, 76%) of CpCr(NO)$_2$(^{15}NO$_2$) with ≥95% isotopic purity as shown by IR analysis. IR (KBr, cm^{-1}): δ_{NO_2} 1359 (s), 1302 (s) (nitro), 1402 (s), 1019 (s) (nitrito).

Quantitative IR Spectroscopy. The data between 1760 and 1880 cm^{-1} were converted from the Mattson Polaris-Icon format to an ASCII format and analyzed by the asymmetric Gaussian curve-fitting program PCFIT using an IBM-compatible 286 computer.[23] The band shapes, relative intensities, and positions of the nitrosyl ν_{NO} absorptions of CpCr(NO)$_2$(NO$_2$) (all ^{14}N) were determined first. The bandwidths for the nitro and nitrito isomers within each symmetric and asymmetric nitrosyl ν_{NO} envelope were constrained to be equal, and the relative intensities of the overlapped nitro/nitrito nitrosyl ν_{NO} absorptions were determined to be 1:5 in CH$_2$Cl$_2$. It is assumed in the calculation of nitro:nitrito ratios from stretching intensities that the nitrosyl ligands of the two linkage isomers possess the same molar absorption coefficients. In the subsequent fitting of the nitrosyl absorptions of CpCr(^{15}NO)(NO)(NO$_2$) and CpCr(^{15}NO)$_2$(NO$_2$), the relative intensities and peak separations for the nitro/nitrito pairs (symmetric and asymmetric) were fixed to the values determined for unlabeled CpCr(NO)$_2$(NO$_2$). The positions of the ^{15}N-labeled ν_{NO} absorptions ([Cr(^{15}NO)$_2$] and [Cr(^{15}NO)(NO)]) were fixed at maxima observed for samples heavily labeled as CpCr(^{15}NO)$_2$(NO$_2$) and CpCr(^{15}NO)(NO)(NO$_2$). The reproducibility of the curve fitting was found to be ±1% at the 99% confidence level.

Reaction of CpCr(NO)$_2$(NO$_2$) with Excess Na^{15}NO$_2$. CpCr(NO)$_2$(NO$_2$) (0.022 g, 0.096 mmol) and Na^{15}NO$_2$ (0.034 g, 0.48 mmol, 5.0 equiv) were stirred in 20 mL of methanol. Periodically, aliquots were removed, taken to dryness, and redissolved in CH$_2$Cl$_2$ for quantitative IR analysis (vide supra).

Reaction of CpCr(NO)$_2$(^{15}NO$_2$) with Na^{14}NO$_2$. A solution of CpCr(NO)$_2$(^{15}NO$_2$) (4 mg, 0.02 mmol) in 4 mL of MeOH was stirred for 3 days, after which time the infrared spectrum showed a statistical distribution of the ^{15}N label. Unlabeled NaNO$_2$ (0.022 g, 0.32 mmol, 21 equiv) was added to the remaining solution, and the reaction was monitored by quantitative IR spectroscopy over a 2-d period.

Kinetic Analysis of CpCr(NO)(^{15}NO$_2$) in the Solid State. A 0.02-g sample of pure CpCr(NO)$_2$(^{15}NO$_2$) was placed in a Schlenk flask under a N$_2$ atmosphere and allowed to stand at 50 °C over a period of 3 d. Periodically, 0.002-g portions were removed and examined by quantitative IR spectroscopy.

First-Order Kinetic Analysis. The initial rate of CpCr(NO)$_2$(^{15}NO$_2$) disappearance was monitored at 24 °C over a 4-d period as a function of concentration of starting complex in methanol (see Table IV).

Eyring Kinetic Analysis of O Atom Transfer. Mixtures containing 0.015 g of CpCr(NO)$_2$(^{15}NO$_2$) and 20 mL of methanol in Schlenk tubes were stirred at 0, 24, 35, and 50 °C with the aid of thermostated baths. One-milliliter aliquots of the solutions were removed at specified times over the period indicated (see Table V) and immediately taken to dryness. The residues were taken up in CH$_2$Cl$_2$ for quantitative IR analysis. Following each completed analysis, the samples were examined by ^{1}H NMR spectroscopy to ensure that no oxidation to CrCr(NO)$_2$(NO$_3$) (δ 5.75, CDCl$_3$) had taken place.

The kinetic runs were repeated using toluene instead of methanol at 23, 36, and 44 °C. As above, aliquots were removed at selected times, taken to dryness, and examined by IR spectroscopy in CH$_2$Cl$_2$ solution.

Reaction of CpCr(NO)$_2$Me with Na^{15}NO$_2$. To a stirred solution of CpCr(NO)$_2$Me (0.018 g, 0.093 mmol) in 10 mL of MeOH was added 0.008 g of Na^{15}NO$_2$ (0.1 mmol, 1.16 equiv). Aliquots of the solution were periodically monitored by infrared spectroscopy to detect any incorporation of the ^{15}N label into the nitrosyl region of the infrared

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(22) Witanowski, M.; Stefaniak, L.; Szymanski, S.; Januszewski, H. *J. Magn. Reson.* **1977**, *28*, 217.

(23) Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50.

spectrum. After 4 d, no incorporation of the ^{15}N label was observed in the nitrosyl absorptions by IR spectroscopy.

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Supplementary Material Available: Listings of observed and predicted powder X-ray diffraction data and a figure showing X-ray powder diffraction patterns for $CpCr(NO)_2(NO_2)$ (3 pages). Ordering information is given on any current masthead page.