1 of 1

Structural Studies of Photoinduced Intramolecular Electron Transfer in Cyclopentadienylnickelnitrosyl

COPY

Lin X. Chen^{*,†}, Michael K. Bowman^{†,§}, Zhiyu Wang^{†,‡}, Pedro A. Montano^{#,◇},
and James R. Norris^{†,‡}

RECEIVED

MAR 21 1984

OSTI

*Contribution from Chemistry Division, Argonne National Laboratory, Argonne,
Illinois, 60439, Department of Chemistry, The University of Chicago, Chicago,
Illinois, 60637, Materials Science Division, Argonne National Laboratory, Argonne,
Illinois, 60439, and Department of Physics, University of Illinois, Chicago, Illinois,
60680*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

875

Abstract: A structural study based on EXAFS, FTIR, and optical absorption spectroscopies has been conducted on a photogenerated, metastable state of cyclopentadienylnickelnitrosyl (CpNiNO) produced by a reversible photochemical reaction. The photogenerated, metastable state with distinctively different EXAFS, IR, and optical absorption spectra from those of the ground state molecules was created by irradiating the sample with the 365 nm line of a mercury lamp at 20K. At the same temperature, the reverse reaction was induced by irradiation with the 313 nm line from the mercury lamp. Based on the analysis of the EXAFS data, the photogenerated, metastable state of CpNiNO has undergone considerable nuclear rearrangements compared to its ground state. The nuclear movement is characterized by a 0.12 Å elongation of Ni-N bond and by a bending of Ni-N-O. A shift of the N-O stretching frequency from 1824 to 1387 cm⁻¹ was observed in the photoinduced reaction with 365 nm light, implying that a NO⁻ like species results from intramolecular electron transfer from Ni to NO. The changes in the absorption spectra for the same reaction showed reduced absorption of the 385 nm band and a newly generated broad band in the near IR region. Temperature dependence of the Debye-Waller factor of CpNiNO was in good agreement with the diatomic harmonic oscillator for the Ni-N bond, but deviated for the Ni-O and the Ni-C bonds. Based on the structures obtained from EXAFS, ZINDO calculations for both the ground state and the photogenerated, metastable state of CpNiNO reproduced the general features of the observed absorption spectra and qualitatively explained the wavelength dependence of the reaction. The calculated partial charges on each atom in the

ground state and the photogenerated, metastable state of CpNiNO are consistent with intramolecular electron transfer upon photoexcitation by 365 nm light.

I. Introduction

Many chemical and biological reactions occur through inter- and intramolecular electron transfer that are often accompanied by nuclear and electronic structural rearrangements. The works of Marcus¹ and others have resulted in significant insight into such electron transfer reactions. However, in order to understand more completely reaction mechanisms and molecular reactivities of electron transfer, a direct structural determination for the molecules undergoing electron transfer is desirable. Facing challenges of short lifetimes and low concentrations of the electron transfer intermediates in chemical reactions, few studies have been conducted in this area. Previous studies by EXAFS (extended X-ray absorption fine structure) on the photodissociation of myoglobin^{2,3} demonstrated the potential of this technique in following structural changes during a chemical reaction, but similar studies on the electron transfer reactions have yet to be done. Expanding on our brief description of the initial effort,⁴ we present here a detailed report of our structural studies of the photoinduced intramolecular electron transfer in CpNiNO. EXAFS, FTIR, optical absorption spectroscopy, and molecular orbital calculations show that the photoinduced intramolecular electron transfer in CpNiNO is coupled with a nuclear rearrangement.

The ground state structure of CpNiNO has been studied extensively with different spectroscopic methods. A microwave spectroscopy of the gas phase CpNiNO⁵ revealed a C_{5v} symmetry of the molecule in the ground state, implying a linear configuration of Ni-N-O. This symmetry is also observed for CpNiNO in a liquid crystal⁶ and in an organic solution⁷. An FTIR investigation on the photochemistry of CpNiNO in an argon matrix at 20K⁸ uncovered a reversible photoinduced intramolecular electron transfer reaction, characterized mainly by a vibrational frequency shift of the N-O stretching. By illuminating the sample with light in the wavelength range from 230 to 280 nm, the intensity of the N-O stretching band at 1832 cm^{-1} for the ground state CpNiNO decreased while a new band at 1386 cm^{-1} appeared. This observation suggested a charge separated $\text{Cp}^-\text{Ni}^{+2}\text{NO}^-$ (Figure 1), because the NO stretching frequency in this photogenerated, metastable state is close to the N-O stretching frequency of NO^- in an argon matrix.⁹ With wavelengths above 290 nm as the illumination source, the band at 1386 cm^{-1} disappeared and the 1832 cm^{-1} band regained its intensity indicating the return of the starting material.⁸ The photogenerated, metastable state has a lifetime up to several hours at 20K. A bent Ni-N-O was predicted in $\text{Cp}^-\text{Ni}^{+2}\text{NO}^-$ according to molecular orbital theory.¹⁰ However, since the precise molecular structure of the charge separated intermediate is lacking, the interpretation of the reaction mechanism and the identity of the metastable state remains unclear.

An EXAFS spectrum shows X-ray absorption modulation as a function of X-ray photon energy above the transition edge of an absorbing atom. The observed

absorption modulations are the result of the wavelength dependence of the interference between outgoing photoelectron waves from the central atom and back scattered photoelectron waves from the surrounding atoms.¹¹ The patterns of the modulations are determined by the types of the atoms involved, the distances between the central atom and its neighbors, as well as the local configuration. EXAFS has the advantage that the local structure can be determined in systems while in noncrystalline forms. Of particular importance to this study, when an intervening atom exists between the absorbing central atom and the back scattering atom, the amplitude of the back scattered wave from the distant atom is enhanced significantly. This is known as the "forward focusing effect".¹² This effect is maximized in a perfectly linear configuration where the angle formed by the central atom, the intervening atom, and the back scattering atom is 180° and diminishes rapidly as this angle deviates from 180° . Therefore, EXAFS is a sensitive technique in characterizing the proposed bent structure of the photogenerated, metastable state of CpNiNO, where the back scattering amplitude of the O atom is expected to drop considerably compared to that of the ground state with a known linear -Ni-N-O configuration.

In this paper, we attempt to demonstrate how the nuclear structure obtained from the EXAFS and the electronic structure obtained from optical and IR spectroscopy complement each other to provide a reasonable understanding for the photochemistry of CpNiNO. Section II includes the experimental and computational details for the study. The results of the structural studies with various methods will be presented in section III. Section IV is devoted to discussions on the mechanism

of the photoinduced intramolecular electron transfer and the origin of the photogenerated, metastable state of CpNiNO. Section V will summarize the results.

II. Experimental and Calculation Methods

Materials and Equipments. CpNiNO was purchased from Strem Chemicals. The 3-methylpentane and n-hexane were from Aldrich. All were used without further purification. The concentration of the 3-methylpentane solution was estimated from the density of the CpNiNO liquid at room temperature and the volume ratio of CpNiNO and 3-methylpentane. The polymer film samples were prepared by mixing CpNiNO liquid with polystyrene solution (dissolved in toluene) and then dried on a piece of aluminum foil (>99%, 0.05 mm thick, Aldrich) inside a nitrogen glove box. The aluminum foil functions as a substrate for heat conduction. The argon gas was from Matheson.

In various experiments included in this paper (except FTIR), the solution sample was held in a specially made cell with an OFHC copper frame and a Mylar or a sapphire window. For EXAFS (and for optical absorption measurements during EXAFS experiments) the cell windows were made of sapphire on one side and of Mylar on the other. For the optical absorption measurements in the UV region, sapphire windows were on both sides of the sample cell. The cell was secured to the cold finger of a Helitran cryogenic system (Air Products). An Au/Fe thermocouple was installed in the

middle of the cold finger. The temperature was monitored and controlled by a Lakeshore temperature controller.

The excitation light source was a 200W mercury lamp (HBO-200W/4) connected with a grating monochromator (Bausch & Lomb). For most of the experiments the entrance and exit slits of the monochromator were 5 mm wide with a FWHM bandpass of about 40 nm. Thus, the spectral purity of the excitation is mainly limited by the intrinsic bandwidth of the mercury lines. The full spectrum ("white light") of the mercury lamp was applied to the sample for the photoinduced reverse reaction.

FTIR. An FTIR study on CpNiNO in an alkane matrix was conducted to confirm the results from previous studies⁸ in the argon matrix, and to explore the photochemistry of CpNiNO in the hydrocarbon solutions in which the EXAFS spectra would be measured.

A Nicolet 510P FTIR spectrometer was used for the IR study. The sample chamber of the spectrometer was modified to fit the Helitran system with KBr windows. A KBr disc held by the OFHC copper holder attached to the cold finger was first cooled to near liquid helium temperature. A solution reservoir was kept at ambient temperature and was connected to the Helitran sample chamber through a valve. A vapor mixture of CpNiNO and n-hexane equilibrated with the solution was then released slowly into the chamber where the mixture immediately condensed on the cold KBr disc. The IR spectra were taken before and after illumination with light at different wavelengths, ranging from 260-545 nm (the discrete lines of the mercury

arc lamp in this region were used). The sample disc plane bisects the right angle formed between the IR light path and the excitation light path. The spectral resolution was 2 cm^{-1} .

Optical Absorption. Optical absorption spectra of CpNiNO in 3-methylpentane solution were taken by a Shimadzu UV-160 spectrometer. The samples were held in the cell with the sapphire window on both sides. For the optical absorption spectra taken during the EXAFS experiments one of the sapphire windows was replaced by a Mylar window. Therefore, only the absorption above 350 nm can be collected without much distortion due to the poor transmission of the Mylar window (nearly zero below 315 nm). The sample plane bisects the right angle formed between the spectrometer light path and the excitation light path.

EXAFS.

a. Light induced charge separation in CpNiNO. The EXAFS measurements were conducted at beamline X-18B of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The Si 220 crystal was used in a double crystal monochromator. The sample (approximately 20 mM 3-methylpentane solution) plane was at a 45° angle with respect to the X-ray incidence with the Mylar window side of the sample cell towards the X-ray beam. The fluorescence detector (EG&G ORTEC HPGe photon detector) was placed at a right angle with respect to the X-ray beam. The sample was kept at near liquid helium temperature with the Helitran system. The excitation light passed through the back of the sample (the sapphire window side).

Ni metal foil was used to calibrate the K-edge energy. Each energy scan required about 20 minutes.

Based on the results of optical absorption and FTIR, the light induced intramolecular electron transfer of CpNiNO is completely reversible and the reaction direction is wavelength dependent (see section III for details). Therefore, the EXAFS scans were collected for four reaction cycles as follows. In each reaction cycle, 10 scans of the CpNiNO without light were collected first, followed by 40 minutes illumination with 365 nm light of the mercury lamp. Next, 10 scans were collected while the sample was illuminated by 365 nm light followed by 30 minutes of "white light" illumination for driving the charge separated CpNiNO back to the ground state. Finally, a new cycle was started by collecting 10 scans on the regenerated ground state sample. Ultimately 40 scans of each for the ground state sample and for the 365-nm light illuminated sample were collected.

b. Effect of temperature and media on CpNiNO structure. The experiments were carried out at beamline X-6B, NSLS. The arrangements were similar to those in beamline X-18B. In addition, the X-ray transmission was collected simultaneously. The solution sample (in 3-methylpentane) had a concentration of approximately 0.8 M and was placed in a cell with aluminum foil on one side instead of the sapphire window as in the last section. The polystyrene film sample had a concentration of around 0.2 M. The argon/CpNiNO gas mixture for the argon matrix isolation experiment was prepared by first allowing CpNiNO vapor to fill a reservoir at room temperature, and then filling the container with argon gas up to a certain pressure.

The CpNiNO/Ar ratio in the mixture is about 1:1000. The gas mixture was then slowly released into the sample chamber and was deposited on the cold aluminum foil attached to the cold finger of the Helitran. The whole deposition time was about 1 hour.

c. **Data analysis.** The parameters for amplitudes and phases were extracted from the reference compounds. Three-shell fits were used for all the CpNiNO data analysis. The parameters from Nickelocene [Ni(Cp)₂] were used as a reference for the Ni-C distance. Because of the lack of a proper Ni-N reference, two sets of parameters from nickelocene and from nickel oxide were used as references in fitting the Ni-N distances. The Ni-N distances listed in this paper are the mid-values of the results from the two sets. The reference for Ni-O is the same as in previous work,^{4,7} where the Co₄(CO)₁₂ parameters were used to model the forward focusing effect for the linear Ni-N-O. For the photoexcited molecule, the same set of parameters was used by assuming that the Ni-N-O bending was less than 30° from the linear such that some multiple scattering remains. This last assumption may generate some minor error in the resulting Ni-O distance in photoexcited CpNiNO. This issue will be discussed later.

According to FTIR and optical absorption results, complete conversion of the ground state CpNiNO to the photogenerated, metastable state was never reached in the experiments. In order to determine the structure of the photogenerated, metastable state of CpNiNO, an EXAFS spectrum of this state must be extracted from that of the 365-nm light illuminated sample where the ground state/photogenerated,

metastable state mixture is present. Because of the overlap between the shells in the Fourier transformed EXAFS spectra, three shells must be simultaneously fit in the data analysis. In this case, the ratio method could not simplify the calculation. The key for obtaining the pure EXAFS spectrum is to determine the correct fraction of the photogenerated, metastable state of CpNiNO in the mixture. Since the ground state spectrum is well known from our previous studies, it was possible to extract the pure photogenerated, metastable state spectrum from a difference spectrum as formulated by $\chi(k) = \chi_m(k) - a \cdot \chi_g(k)$, where a is the fraction of the ground state in the mixture, and m and g stand for mixture and ground state, respectively. The two sets of the spectra, $\chi_m(k)$ and $\chi_g(k)$, were carefully normalized based on the jump height at the Ni edge. The resulting spectra, $\chi(k)$, were fit to a three-shell model with the EXAFIT program. If the resulting spectra $\chi(k)$ have contributions from both the ground state and the photogenerated, metastable state molecules, the three-shell model will not fit properly because of the difference in the nuclear positions in the two states. When the a value was too large, the baseline of the resulting spectrum was no longer flat and new oscillation peaks due to oversubtracting would emerge. Again, the resulting spectrum would not fit a three-shell model. The most probable a value was determined when the least standard deviation was reached from the three-shell fit. More details will be discussed in section III.

For EXAFS studies of CpNiNO in different media and at different temperatures, the same EXAFS analysis programs were used. The normalized spectra at different temperatures were analyzed with a set of fixed coordination numbers. The resulting

Debye-Waller factors were modeled with the harmonic oscillator for diatomic molecules.¹³

ZINDO calculation. The program ZINDO was a part of the Personal CAChe package from Tektronix. The molecular structures of the ground state and the photogenerated, metastable state of CpNiNO from the EXAFS results were used in the calculation. The eigenvalues and eigenvectors were calculated for both the ground state and the photogenerated, metastable state. The electronic transition dipoles and the optical absorption spectra were also calculated for both structures. The restricted Hartree-Fock calculations were used for both the ground state and the photogenerated, metastable state of CpNiNO. Forty-two atomic orbitals (AO's) were used to form a STO basis set for the forty-two molecular orbitals (MO's) in the calculations. The AO's consist of 3d, 4s, and 4p orbitals from Ni, 2s, and 2p orbitals from N, O, and C, as well as 1s orbitals from H. The partial charges at each atom and the bond orders were also calculated for both structures. Calculations for the structures of the first excited singlet and triplet states were carried out via the open shell restricted Hartree-Fock method.

III. Results

Before the results and discussions are presented, the names for different CpNiNO species involved in the photochemical reaction in Figure 1 need to be clearly defined. The two structures shown in Figure 1 are called the ground state or the linear CpNiNO and the photogenerated, metastable state or the bent CpNiNO. The

"metastable state" is attached to the name for the latter because this species can be converted back to the ground state by illuminating the sample with 313 nm light or by simply warming up the sample to over 100K. The "365 nm light illuminated sample" is used to imply a mixture of the ground state and the photogenerated, metastable state of CpNiNO.

FTIR Study on CpNiNO in n-Hexane Matrix. The FTIR spectra of CpNiNO in the n-hexane matrix described earlier are shown in Figure 2. Because most of the CpNiNO vibrational bands overlap with those of the n-hexane matrix, it is difficult to characterize the structural changes in those regions due to the low concentration of CpNiNO relative to n-hexane. However, a very strong N-O stretching band in the ground state CpNiNO is at 1824 cm^{-1} in the hexane matrix where no other vibrational bands are present. Thus, this band was used to characterize the structural changes in CpNiNO as in previous IR studies.⁸ The N-O stretching frequency in the hexane matrix appeared 8 cm^{-1} lower than the 1832 cm^{-1} reported for the argon matrix isolated CpNiNO,⁸ implying interactions between CpNiNO and the hexane matrix. Similar to that in the argon matrix, a N-O stretching frequency shift of about 440 cm^{-1} was also observed in the hexane matrix isolated CpNiNO upon illumination with the mercury lines in the 260-290 nm. Thus, the intensity of the ground state N-O stretching band at 1824 cm^{-1} decreased, while a new band at 1387 cm^{-1} emerged. Following illumination with the mercury lines at 302 and 313 nm, the reverse reaction was induced characterized by the disappearance of the new band at 1387 cm^{-1} and the recovery of the 1824 cm^{-1} band to its initial intensity. The sample in the hexane

matrix was also illuminated with other mercury lines in order to characterize the wavelength dependence of this photoinduced reaction. The intensity of the N-O stretching band at 1824 cm^{-1} was used to monitor the effect after illumination with each mercury line. The results were qualitative because the relative intensities of the mercury lines were different. The experiment, at this time, is limited by the availabilities of the mercury lines. It was found that in addition to the mercury lines below 290 nm, 365 and 435 nm lines could also cause the same N-O stretching frequency shift, whereas 334 and 545 nm lines induced the reverse reaction. Figure 2 shows the IR spectra before and after illumination with the 365 nm light as well as the difference spectrum. The 1824 cm^{-1} band intensity only decreased by about 25% even after long exposure to the 365 nm light, which indicated a partial conversion of the ground state to the photogenerated, metastable state of CpNiNO. This may be due to the following reasons; (1) the 365 nm light could only penetrate the top layer of the sample because the hexane matrix was too thick and frosty; (2) the photogenerated, metastable state of CpNiNO may also absorb light in the same region resulting in the steady-state equilibrium of the two states.

The downshift of the N-O stretching frequency indicates a weakening of the N-O bond which results from the extra electron transferred from Ni to the N-O antibonding π^* orbital. The N-O stretching frequency of the photogenerated, metastable state of CpNiNO at 1387 cm^{-1} is close to the frequency of the matrix isolated NO^- ,⁹ which supports the intramolecular electron transfer hypothesis. Although there is no definite correlation between the N-O stretching frequency and

Ni-N-O angle, the 1387 cm^{-1} is much too low for a linear Ni-N-O.¹⁰ A bridging Ni-N-O is not likely because of the dilution in the argon or alkane matrix. Thus, the only possibility of having the N-O stretching at 1387 cm^{-1} appears to be a bent Ni-N-O.

Optical Absorption. The optical absorption spectra of CpNiNO in 3-methylpentane solution are shown in Figures 3 and 4. The spectra in Figure 3 resemble those shown in previous studies on the argon matrix isolated CpNiNO⁸ with a band at 280 nm. The band at 200 nm from previous studies⁸ was well characterized due to the cut-off of the spectral range of the spectrometer. The spectra in Figure 3 were taken at 20K on the sample which became a shattered glass; thus, the background contained contributions from the scattered light. There was a spectral red shift of the 280 nm band as indicated by the difference spectrum in Figure 3(c). Because of the poor optical quality of the shattered sample, the spectral changes can only be characterized qualitatively.

Figure 4(a) shows the optical absorption of CpNiNO (20 mM 3-methylpentane solution) in the region of 350-1000 nm at 20K. The sample concentration here was at least 100 times higher than that in Figure 3. The absorption spectrum in this region features two bands peaked at 385 and 462 nm, which were not apparent in the spectrum of the previous argon matrix isolation study⁸ and in Figure 3 due to low concentrations. The spectra in Figure 4 were measured during the EXAFS experiments where the sample was in a cell with a Mylar window on one side. Therefore, the absorption spectra below 350 nm is truncated. The absorption spectrum of the ground state in this region explained the previous observation⁸ that

the charge separation of CpNiNO could be induced by light with wavelengths up to 400 nm. The absorption bands in the 300-600 nm region also agree with our FTIR results for the wavelength dependence of the photoinduced reaction. After a 40 minute illumination with 365 nm light at 20K, changes in the absorption spectrum of the sample occurred, featuring a reduced 385 nm band intensity and a rising broad absorption band centered at 850 nm. When the 313 nm mercury line or all mercury lines were subsequently used to illuminate the sample, the reverse reaction was observed characterized by the recovery of 385 nm band and the disappearance of the broad band in the 800-1000 nm region. Considering the relative intensity of the 313 nm band to that of the 365 nm band (about 1:8), the back reaction was induced much more effectively compared to the forward reaction. Thus, illumination with "white light" from the mercury lamp caused almost complete recovery of the ground state.

It is worth noting that certain structures appeared in the broad absorption band in the near infrared region for the photoexcited sample (Figure 4). A few small peaks with their energy interval of about 700 cm^{-1} are contained in the broad band. This may imply that a particular vibronic transition with energies far away from other transitions is dominant for the absorption in this region. We will discuss the possible reasons why this particular transition is only active in the bent CpNiNO later.

EXAFS Spectra. The EXAFS spectra for CpNiNO are shown in Figure 5. Figure 5a shows the spectrum for the ground state CpNiNO sample. Figure 5b is the spectrum of the sample after 40 minutes illumination with the 365 nm mercury line.

Because of incomplete conversion of the ground state to the photogenerated, metastable state of CpNiNO, this spectrum (Figure 5b) results from a mixture of the two species. Figure 5c was taken after subsequent illumination with "white light" from the mercury lamp. The resemblance of Figures 5a and 5c verifies the reversibility of the reaction depicted in Figure 1. The Fourier transform of the spectra in Figures 5a and 5b are shown in Figure 6 where a shift of the Ni-N/Ni-C peak and a reduction in the amplitude of the Ni-O peak are observed for the 365 nm light illuminated sample relative to the ground state CpNiNO. Since the enhancement of O atom back scattering will be at its maximum when Ni-N-O is perfectly linear, the reduction of the O atom back scattering amplitude indicates that a bent Ni-N-O configuration has been created upon 365 nm light illumination.

The atom-to-atom distances of the ground state CpNiNO at 20K is almost the same as those in the previous EXAFS study at room temperature.⁷ The Ni-N, Ni-C, and Ni-O distances in the ground state CpNiNO are 1.65 ± 0.03 , 2.15 ± 0.02 , and 2.78 ± 0.04 Å, respectively.

To determine the atom-to-atom distances for the photogenerated, metastable state of CpNiNO, the EXAFS spectrum for the pure metastable state must be extracted from the spectrum of the mixture in Figure 5b. As mentioned in the Experimental section, the pure photogenerated, metastable state spectrum was extracted from the difference spectrum by subtracting a fraction of the ground state spectrum from that of the mixture. Comparing the EXAFS spectra of the two states, the most noticeable difference occurs around $k = 4$ Å⁻¹ (see Figures 5a and 5b), where

the oscillation peaked at a much higher amplitude for the ground state than that for the mixture. As the fraction of the ground state spectrum subtracted from that of the mixture increases, the oscillation peak at $k = 4 \text{ \AA}^{-1}$ becomes less distinctive in the resulting difference spectrum. When the fraction of the ground state ranges from about 0.55 to 0.60, this peak at $k = 4 \text{ \AA}^{-1}$ diminishes completely in the resulting spectrum where a smooth oscillation curve with a flat baseline can still be seen (middle spectrum in Figure 7). A further increase in the ground state fraction produces a fluctuating baseline and new oscillations in the resulting spectrum, indicating oversubtraction.

The nonlinear least square fittings with a three-shell model were conducted on the difference spectra resulting from subtracting different ground state fractions. When both the ground state and the photogenerated, metastable state of CpNiNO coexist in the difference spectrum after the subtraction, the fit with a three-shell model is not proper because of the structural heterogeneity. If oversubtracted, the resulting difference spectrum will again not fit a three-shell model because of the distortion in the baseline. The results of the fits are shown in Figure 7. The standard deviation, as a function of the ground state fraction a , is shown in Figure 8. The results indicate that the most proper fraction of the ground state CpNiNO in the mixture is around $57 \pm 3\%$. This agrees with our observation based on the appearance of the resulting difference spectra as a function of the ground state fraction a as mentioned earlier. Therefore, the middle spectrum in Figure 7 is very close to that of the pure photogenerated, metastable state of CpNiNO.

Table I lists the structural parameters of CpNiNO in both the ground state and the photogenerated, metastable state. The fit with a three-shell model for the photogenerated, metastable state of CpNiNO gives distances of $2.15 \pm 0.02 \text{ \AA}$ and $1.77 \pm 0.03 \text{ \AA}$ for Ni-C and Ni-N, respectively. The $0.12 \text{ \AA}$ elongation of the Ni-N bond in the photogenerated, metastable state is the source of the peak shift observed in the Fourier transform EXAFS spectra in Figure 6 for the 365 nm light illuminated mixture. The lengthened Ni-N bond also implies a decrease of the bond order resulting from intramolecular electron transfer from Ni to NO. Little change observed in the distances of Ni-C for the photogenerated, metastable state molecules as compared to that for the ground state, implies that the molecular orbitals contributing to the bonding between Ni and C are not greatly involved in photoinduced electron transfer.

The Ni-O distance in the photogenerated, metastable state of CpNiNO has a greater uncertainty as compared to that of the ground state for the following two reasons. (1) Lacking a reference compound for Ni-N-O, the Ni-O distances determined for the ground state and the photogenerated, metastable state of CpNiNO rely on the reference phases obtained from Co-O in $\text{Co}_4(\text{CO})_{12}$, which result from both linear and slightly bent Co-C-O. Thus, it may not be the ideal reference for the bent Ni-N-O. (2) The reduced signal-to-noise level in the Ni-O component of the difference spectrum may contribute additional error to the Ni-O distance determination. Thus, the Ni-O distance approximated for the photogenerated, metastable state as $2.82 \pm 0.04 \text{ \AA}$, likely has uncertainty additional to that indicated by the standard deviation. Two extremes of N-O distances were used to estimate the bond angle Ni-N-O. Assuming

the N-O distance of the photogenerated, metastable state of CpNiNO to be in the range of 1.13 Å (extracted from the ground state structure) to 1.26 Å (from NO⁻), the bond angle of Ni-N-O is within the range of 134-152°.

In the ground state CpNiNO, the Ni and NO are linked by a σ bond formed via a donation of electron density from NO to Ni, and by a π bonding via a donation of electron density from d_{xz}/d_{yz} orbitals of Ni to the empty π^* orbital of NO (in the ground state, the NO is considered NO⁺), so called "back bonding". As the photoinduced intramolecular electron transfer occurs, the electron density increases in the π^* orbital, destabilizing the N-O bonding. Thus, the N-O bond is weakened, leading to a lower N-O stretching frequency compared to that at its ground state. Meanwhile, in order to minimize the destabilization, the Ni-N-O has to bend such that the overlap between the antibonding d_{xz}/d_{yz} and π^* is reduced. Both effects agree with our observations of the N-O stretching frequency downshifting and the Ni-N bond length increasing.

The X-ray absorption at the near edge of the sample before and after the 365 nm light illumination was examined carefully. There was neither an apparent edge shift (< 0.5 eV) nor a change in the shape of the spectrum in this region upon illumination, despite the fact that some changes were expected as a result of the electronic structural change. However, the changes might be too small to observe or are masked because of incomplete conversion to the photoexcited CpNiNO intermediate.

Effect of Temperature and Media on the structure of CpNiNO. The EXAFS spectra of CpNiNO in 3-methylpentane at different temperatures are shown in Figure 9. The reduction of the oscillation amplitude as a function of temperature indicates the increase of the disorder in the molecules at higher temperatures. The Debye-Waller factor differences as a function of temperature using $T = 4\text{K}$ as a reference temperature are shown in Figure 10. The smaller Debye-Waller factor differences for the Ni-N shell at all temperatures indicated a tighter bonding of Ni-N as compared to Ni-C. However, the largest Debye-Waller factor differences are found in Ni-O, which can be easily interpreted by an indirect bonding between Ni and O. Figure 10 also shows that the harmonic oscillator model¹³ for the diatomic molecule approximates the behavior of the Debye-Waller factor of Ni-N very well, whereas the discrepancy increases for Ni-C and Ni-O. This is because Ni-N distance can be affected only by Ni-N stretching mode, whereas multiple vibrational modes are involved in the Ni-C and Ni-O distances. For example, the Ni-C distance will be affected by the Ni-ring stretching, the tilt, and the ring vibrations, and the Ni-O distance, by the Ni-N stretching, the N-O stretching, and the Ni-N-O bending. These combined effects are considerably more complicated than the single Ni-N stretching mode. The structural parameters of CpNiNO in the argon matrix (10K) and in the polymer films (at different temperatures) are very close to those in the solution at 10K, even though some differences were observed at the near edge region. The temperature dependence of the back scattering amplitudes for the polymer films are much less apparent compared to those of the solution sample.

ZINDO Calculation. The ZINDO calculations were conducted for both the linear and the bent CpNiNO with the structures from EXAFS data analysis. The calculations were focused on those related to the experimentally observed properties and on understanding the mechanism of the reaction in Figure 1. A few calculations of electronic structures have been done^{14,15} for the ground state of CpNiNO with the linear Ni-N-O arrangement. The eigenvalues of the MO's for the linear CpNiNO in our calculations are similar to those in previous work¹⁵ with minor differences. The dominant components of the MO's in terms of the frontier orbitals (e.g., 4s, 4p, 3d orbitals of Ni, π orbitals of Cp, and n , π^* orbitals of NO) are the same as those in earlier studies.¹⁴ The correlation MO diagrams for those orbitals near HOMO and LUMO are shown in Figure 11. The main differences in MO energies between the linear and the bent molecules occur to the LUMOs, where the two degenerate antibonding orbitals in the linear CpNiNO lowered their energies and split into two orbitals with the energy difference of 0.41 eV compared to that of 0.03 eV for the linear CpNiNO. The two LUMO's of the linear CpNiNO are constructed mainly from Ni d_{xz}/d_{yz} with NO π^* and minor contribution from $4P^*$. Therefore, when Ni-N-O bends, the energy of the MO with d_{yz} and p_y^* drops because of less overlap between the antibonding orbitals (see Figure 11) compared to that in the linear CpNiNO. Table II lists the calculated partial charges and the bond orders of the linear and bent CpNiNO based on the structures from EXAFS data analysis. The partial charge and the bond order changes due to the Ni-N bond elongation and the Ni-N-O bending, demonstrate the intramolecular electron transfer as expected where the charge on Ni

becomes more positive and that on N becomes more negative in the bent CpNiNO compared to those in the linear CpNiNO.

Although the calculated spectra for both the linear and the bent CpNiNO in Figure 12 deviate in the absolute positions of the observed absorption bands, they qualitatively reproduce important general spectral features observed in the experimental measurements. Although shifted to near 200 nm in the calculated spectra (Figure 12), a red shift was reproduced for the bent CpNiNO relative to the linear molecule as observed in Figure 3 for the 280 nm band. Meanwhile, the broad absorption band in the near infrared region for the bent CpNiNO is reproduced in calculated spectrum (Figure 12) similar to that observed in the experiment (see Figure 4). According to the results of the electronic transitions by the CI calculation, the appearance of the absorption in the near infrared region for the bent CpNiNO is the direct consequence of lowering and splitting the energies of the two LUMO orbitals shown in Figure 11. The corresponding transitions for the linear CpNiNO occur in a shorter wavelength region (600-700nm) and are much weaker compared to the bent CpNiNO. The calculated electronic spectra in the UV region in Figure 12 can be used to interpret the wavelength dependence of the reaction in Figure 1. The calculated transitions for the linear CpNiNO at around 190 nm corresponds to the observed ground state absorption band at around 280 nm. The bent CpNiNO has transitions red-shifted by about 10 nm from those for the linear CpNiNO. The transition dipole calculations revealed that the transitions for the linear CpNiNO at 190 nm correspond to the transfer of the electron density from Ni to NO, whereas the transitions for the

bent CpNiNO centered at 200 nm transfer the electron density from NO to Ni. In addition, according to the calculations, electronic transitions for the bent CpNiNO in the near IR region produce a net electron density transfer from NO to Ni. In the following session, the implications of the findings from the experimental and calculated results will be discussed.

The energy minimized structures of the first excited singlet and triplet states of CpNiNO still gave a linear Ni-N-O configuration even though the other bond length parameters were changed.

IV. Discussions

Origin of the Photogenerated, Metastable State of CpNiNO. The key to understanding the mechanism of the photochemical reaction in Figure 1 is identifying the origin of the photogenerated, metastable state of CpNiNO. In previous photolysis studies of CpNiNO in the argon matrix,⁸ a hypothesis was made for the origin of the intermediate. The ion pair $[\text{CpNi}]^+ \text{NO}^-$ intermediate due to the photoionization was ruled out because the photon energy required to initiate the reaction was much lower ($> 1\text{eV}$ lower) than the minimum estimate for the photoionization. The other possible origin of the photogenerated, metastable state of CpNiNO was suggested as $\text{Cp}^- \text{Ni}^{+2} \text{NO}^-$, an intermediate due to photoinduced intramolecular electron transfer from Ni to NO. In general, the bonding between Ni and NO is considered to have two contributions, σ bonding formed by NO electron donation to the Ni, and π bonding created by the overlap of the d orbitals of Ni with the antibonding π^* orbitals of NO.

As a consequence of transferring two electrons from the d orbitals of Ni to the π^* orbitals of NO, the bonding character for Ni-N bond is reduced, while the antibonding character of N-O bond is increased. The Ni-N bond elongation and Ni-N-O bent observed from the EXAFS results agree with this hypothesis. Although the intramolecular electron transfer hypothesis fits the observation of the structural changes in CpNiNO upon going from the ground state to the photogenerated, metastable state, whether the reaction in Figure 1 can be described by a single-step model involving only these two states is far from clear. The ambiguity comes from (1) the extremely long lifetime of the photogenerated, metastable state at 20 K, (2) the wavelength dependence of the reaction, and (3) the still linear Ni-N-O configuration from the calculated structure of CpNiNO at its first excited singlet and triplet states by ZINDO.

The lifetime of the photogenerated, metastable state of CpNiNO in our study was as long as a few hours below 70K. The recovery of the sample in the dark to its ground state took place as the 3-methylpentane glass matrix started to thaw. It is very strange for an electronically excited state generated directly by the photoexcitation to have such a long lifetime, and for a two electron transfer reaction to be completed in one step. Thus, the simple two-state model is not sufficient here to explain adequately the reaction. Therefore, a kinetics study of this reaction in a time-resolved fashion may give a hint to the existence of any transition state between the linear and the bent CpNiNO. If a transition state with an electronic structure different from the bent CpNiNO has a different transient absorption spectrum from

those of the ground state and the long-lived bent intermediate, the existence and properties of this state may be established with transient absorption spectroscopy. In addition, the correlation between the lifetime of the bent intermediate and the reaction temperature will also help to reveal the mechanism of the reaction. We plan to study these aspects in the future.

The question of the origin of the bent CpNiNO intermediate arises as we consider the fact that the forward and the reverse reaction shown in Figure 1 can be induced respectively by lights with the energy difference as small as 2400 cm^{-1} (280 nm for the forward reaction vs. 300 nm for the reverse reaction). If only two states are involved in the reaction in Figure 1, the potential energy surfaces for the ground and the excited state must cross each other. Thus, the 2400 cm^{-1} would have to be the energy difference between the potential surface minimum of the two states, which is much too low for any two electronic states in the same molecule. Therefore, the wavelength dependence of the reaction in Figure 1 suggests that at least one other state is involved in the reaction and the bent CpNiNO is likely a structure relaxed from the initially excited state. According to the ZINDO calculation, the two transitions from the two occupied e_1 MO's (consisting of Cp e_1 and Ni e_1 orbitals) to the e_1 LUMO (antibonding d_{xz}, d_{yz} of Ni and antibonding π of NO) are responsible for the charge separation induced by the UV light below 280 nm. The transitions from the e_2 and a_1 MO's (consisting of Ni e_2 and a_1 orbitals) to the LUMOs, although rather weak, are the reasons for the charge separation of CpNiNO induced by 365 nm light. In both cases, the final electronic structures after the transition are different

from those obtained from the ZINDO calculation for the bent molecule. In other words, the immediate end products of these transitions are not bent CpNiNO. In addition, the very long lifetime of the bent CpNiNO cannot be justified by the electronic structural change from the above transitions. Thus, the calculations also suggest at least one transition state between the linear and the bent CpNiNO. The identity of this transition state can be revealed only when the dynamics of the reaction is clear and the proper transition state electronic structure is available. At this time, we can only conclude that the reaction shown in Figure 1 has to go through some intermediate between the linear and the bent CpNiNO and that the bent CpNiNO can be created only when there is an intermediate state. This also agrees with the fact that the calculated structure for the first excited singlet and triplet states of CpNiNO remains a linear Ni-N-O configuration. This suggests that the bent CpNiNO is unlikely the first excited singlet or triplet state, and that the reaction may have to undergo a two-step intramolecular electron transfer to reach the bent CpNiNO metastable state.

Photoselectivity of the Reaction. The excitation wavelength dependence of the reaction in Figure 1 has been mentioned in the previous photochemistry study in the argon matrix.⁸ However, the actual cause of such wavelength dependence was not clear. As we obtain the structures for the linear and the bent CpNiNO, the electronic transitions can be calculated which should provide the answer to this puzzle.

In order to answer this question, the origins of the electronic transitions causing the reaction to proceed one way or the other for both the linear and the bent CpNiNO

should be discussed. For the ground state CpNiNO, the optical absorption spectrum features two strong absorption bands in the UV region centered at 200 and 280 nm (only the 280 nm band is shown in Figure 3 due to the limitation of the spectrometer), respectively, and two weak absorption bands at 385 and 460 nm with a large overlap between them. According to our limited results for the wavelength dependence of the reaction (limited by the mercury lines) depicted in Figure 1, the excitation in both regions (e.g., 280 and 365 nm) causes the forward reaction. For the bent CpNiNO, the absorption spectrum from 200-600 nm is ambiguous because the incomplete conversion from the ground state to the photogenerated, metastable state results in optical absorption from both species. However, the absorption in the near infrared region from the photogenerated, metastable state of CpNiNO is very clear since no absorption from the ground state CpNiNO is observed in this region.

The quantum mechanical calculations are helpful in obtaining the origin of the electronic transitions. One important result from previous work^{14,15} indicated the mixing of two e_1 orbitals of Ni, e.g., d_{xz}/d_{yz} and p_x^*/p_y^* . The resulting two stable e_1 orbitals interact with e_1 of Cp and e_1 of NO (π^*), respectively, forming two occupied e_1 orbitals with different energies and two empty e_1^* orbitals. Our calculated results for the linear CpNiNO showed similar mixing between these orbitals. The two occupied e_1 orbitals along with a_1 , e_2 orbitals form the frontier orbitals of the reaction shown in Figure 11. Although calculated spectra sometimes deviate from what is observed experimentally, the similarity of the general features of the calculated and observed spectra in the UV region and the near infrared region are unambiguous.

Thus, a one-to-one correspondence can be made between the observed 280 nm band and the calculated 192 nm band for the linear CpNiNO. We will discuss the origin of this absorption band, as well as that for the broad absorption in the near infrared. According to the CI calculation, the broad band absorption in the near infrared region for the bent CpNiNO is due to the transitions from HOMO e_1 to LUMO $a_1'^*$ (see Figure 11). The corresponding transitions in the linear ground state of CpNiNO, from HOMO e_1 to LUMO e_1^* , have higher energies of around 600-700 nm and are much weaker than those for the bent CpNiNO in the near infrared region. The net electron density change, due to the transitions in the near infrared region for the bent CpNiNO, is moving the electron density from the π^* orbitals of NO to the antibonding orbitals of Ni. This would be consistent with the electron movement in the photoinduced reverse reaction. Thus, one can predict that illumination with near infrared light on the bent CpNiNO will cause the reverse reaction. The calculated absorption spectra in the region of 300-700 nm for both states do not show a clearcut resemblance with experimental observations. Since the transitions in this region are very weak, some ambiguity exists for the spectra in this region and will not be further discussed. Nevertheless, the calculated transitions from the 300-500 nm for the linear CpNiNO are mainly due to the transitions from the $a_1 e_2$ MO's (consisting of Ni $d_{x^2-y^2}$, d_{xy} and d_{z^2}) to the LUMO e_1 . These transitions are very weak compared to those in the UV and the near infrared regions because of the symmetry requirements for the transitions. For the linear CpNiNO, the net electron density change due to any of these transitions favors the electron transfer in the forward reaction, i.e., from Ni to

NO. These calculated results qualitatively agree with the observation that the 385 and 460 nm bands in the linear CpNiNO are much weaker than those in the UV region, and the illumination in this region cause the forward reaction. The calculated absorption band for the linear CpNiNO near 192 nm is due to the transitions from the e_1 orbitals (the lowest one in Figure 11) to the LUMO e_1 . The net electron density change upon this transition also favors the forward reaction in Figure 1 similar to those calculated transitions in the 300-500 nm region. For the bent CpNiNO, a dominant band at around 200 nm slightly red shifted from that of the linear CpNiNO, is mainly due to the transitions from the HOMO e_1 to the higher unoccupied e_1 orbitals (not shown in Figure 11) constructed from the antibonding e_1 's of Cp and Ni. The net electron density changes accompanying the transition results in depletion of the electron density from NO to Ni, causing the reverse reaction in Figure 1. Although the observed absorption peak for the ground state CpNiNO is located at 280 nm, the similarity of the general features in this spectral region between the calculated and the observed spectra suggests the assignment of the 192 nm band in the calculated spectrum to the 280 nm peak in Figure 3. The origins of the transitions at 192 nm for the linear CpNiNO and at 200 nm for the bent configuration show clearly the observed photoselectivity of the reaction where the light of 230-280 nm caused the forward reaction and the light around 300 nm caused the reverse reaction.

V. Summary

A series of structural studies of CpNiNO have demonstrated that its nuclear rearrangements are coupled to its electronic transitions as photoinduced intramolecular electron transfer occurs. The nuclear structure of the photogenerated, metastable state of CpNiNO obtained from EXAFS studies indicated a 0.12 Å Ni-N bond elongation and considerable Ni-N-O bending. These structural changes in CpNiNO, resulting from intramolecular electron transfer, agree with the observed IR and the optical absorption spectra of CpNiNO in the ground state and in the photogenerated, metastable state. The structural changes also fit the intramolecular electron transfer description of the reaction in Figure 1. Based on the EXAFS structures of CpNiNO for both states, the electronic structures and the electronic spectra of CpNiNO are calculated. The calculated electronic structures are consistent with intramolecular electron transfer from Ni to NO in the forward reaction of Figure 1. The calculated spectral behavior for both structures reproduces the general features of the observed absorption spectra, and can be used to explain qualitatively the photoselectivity of the reaction and to probe the origin of the photogenerated, metastable state of CpNiNO. The calculations and the kinetic behavior of the photogenerated, metastable state of CpNiNO suggest the existence of at least one transition state in the reaction path. The confirmation of this hypothesis is to be explored through future time-resolved spectroscopic studies.

Acknowledgement

We would like to thank Professor Jerome Burdett from the University of Chicago for his suggestion of CpNiNO and for his inspiring discussions. The assistance of X-18B and X-6B beamline personnel at NSLS is also greatly appreciated. We would like to thank Dr. Farrel Lytle for allowing us to use the $\text{Co}_4(\text{CO})_{12}$ spectrum. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, the Division of Chemical Sciences, and the Division of Materials Science under contract W-31-109-Eng-38.

REFERENCES:

[†]Chemistry Div., Argonne National Laboratory, Argonne, Illinois, 60439

[‡]Dept. of Chemistry, The University of Chicago, Chicago, Illinois, 60637

[#]Materials Science Div., Argonne National Laboratory, Argonne, Illinois, 60439

[◇]Dept. of Physics, University of Illinois, Chicago, Illinois, 60680

[§]Present address: Pacific Northwest Laboratory

(1) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155-196.

(2) Chance, B.; Fischetti, R.; Powers, L. *Biochemistry* **1983**, *22*, 3820-3829.

(3) Powers, L.; Sessler, J. L.; Woolery, G. L.; Chance, B. *Biochemistry* **1984**, *23*, 5519-5523.

(4) Chen, L. X.; Bowman, M. K.; Montano, P. A.; Norris, J. R. *J. Am. Chem. Soc.* **1993**, *115*, 4373-4374.

(5) Cox A. P.; Brittain, A. *Trans. Faraday Soc.* **1970**, *66*, 557-562.

(6) Beattie, I. R.; Emsley, J. W.; Sabine, R. M. *J. Chem. Soc. Faraday Trans.* **1974**, *70*, 1356-1363.

(7) Chen, L. X.; Bowman, M. K.; Thurnauer, M. C.; Lytle, F. W.; Norris, J. R. *Chem. Phys. Lett.* **1992**, *200*, 290-296.

(8) Crichton, O; Rest, A. J. *J. Chem. Soc. Dalton Trans.* **1977**, *10*, 986-993.

(9) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1971**, *55*, 3404-3418.

(10) Richter-Addo, G. B.; Legzdins, P. *Metal Nitrosyl*; Oxford University Press: New York, 1992.

(11) (a) Sayers, D. E.; Stern, E. A.; Lytle, F. W. *Phys Rev. Lett.* **1971**, *27*, 1204-1207. (b) Stern, E. A.; Sayers, D. E.; Lytle, F. W. *Phys. Rev. Lett.* **1975**, *11*, 4836-4846.

(12) (a) Teo, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 3990-. (b) Boland, J. J.; Crane, S. E.; Baldeschwieler, J. D. *J. Chem. Phys.* **1982**, *77*, 142-.

(13) Teo, B. K. *EXAFS: Basic Principles and Data Analysis*; Springer-Verlag: New York, pp. 91-101, 1986.

(14) Orgel, L. E. *J. Inorg. Nucl. Chem.* **1956**, *2*, 315-322.

(15) Böhm, M. C. *Z. Naturforsch.* **1981**, *36a*, 1361-1366.

FIGURE CAPTIONS:

Figure 1. Photochemical reaction of CpNiNO.

Figure 2. FTIR and difference spectra of CpNiNO in n-hexane matrix at 20K in two frequency regions, for the ground (solid) and photoilluminated (dashed) samples. The main peak in (b) is from a symmetric bending mode of the $-CH_3$ group in n-hexane. A new "shoulder" appeared at the right side of the peak upon illumination and is from N-O stretching in the photogenerated, metastable state of CpNiNO.

Figure 3. Optical absorption spectra of CpNiNO (3-methylpentane solution at 20K) in the UV region a) before, b) after 365 nm illumination, and c) difference of a) and b). Since the 3-methylpentane solution forms a shattered glass at near liquid helium temperature, the baselines of the optical absorption spectra are affected by scattered light.

Figure 4. Optical absorption spectra of CpNiNO (3-methylpentane solution at 20K, in the sample cell with one Mylar window) in visible and near infrared region.

Figure 5. EXAFS spectra of CpNiNO (20 mM 3-methylpentane solution at 20K), a) before, b) after 40-minute 365 nm, and c) after subsequent "white light" illumination. The likeness of a) and c) confirmed the reversibility of the reaction.

Figure 6. FFT EXAFS spectra of CpNiNO (3-methylpentane solution at 20K), before (solid), and after (dashed) 40-minute 365 nm illumination.

Figure 7. The three-shell model fits (x) and the experimental (solid) EXAFS spectra for CpNiNO. The bottom solid curve is the same as in Figure 5(b) and the cross symbols are constructed from the fitting parameters for the ground state and the photogenerated, metastable state of CpNiNO, with a relative ratio of 57:43.

Figure 8. The standard deviations of three-shell fits for the difference EXAFS spectra $\chi(k)$ vs. the ground state fraction, a . (See text.)

Figure 9. The EXAFS spectra of CpNiNO in 3-methylpentane at different temperatures with k^2 weighting.

Figure 10. The Debye-Waller factor differences for CpNiNO in 3-methylpentane at different temperatures. The circles are experimental values extracted from the three-shell fits. The solid lines are calculated from a harmonic oscillator model with diatomic molecule approximation.

Figure 11. The orbital correlation diagrams for the frontier orbitals of the linear and the bent CpNiNO.

Figure 12. The calculated electronic spectra of CpNiNO based on the EXAFS structure of the linear and the bent CpNiNO. The vertical scale of the bottom spectra has been enlarged 166 times compared to the top spectra.

Table I. Structures of CpNiNO from EXAFS Data Analysis

Table II. ZINDO Calculations of Partial Charges and Bond Orders for the Linear and the Bent CpNiNO.

Table I. Structures of CpNiNO from EXAFS Data Analysis (20 mM in 3-methylpentane, 20K)

Distance (Å)	Ground State	Photogenerated, metastable State
Ni-N	1.65 ± 0.03	1.77 ± 0.03
Ni-C	2.15 ± 0.02	2.15 ± 0.02
Ni-O	2.78 ± 0.04	2.82 ± 0.04
Bond Angle (°)		
Ni-N-O	180	134-152 ^a

^aAssuming NO distance is in the range of 1.13-1.26 Å.

Table II. ZINDO Calculations of Partial Charges and Bond Orders for the Linear and the Bent CpNiNO.

Partial Charges			Bond Orders		
	Linear	Bent		Linear	Bent
Ni	+0.8	+1.0	Ni-N	1.8	1.0
N	-0.1	-0.3	N-O	1.6	1.4
O	-0.4	-0.4	Ni-C	0.4	0.4
C	-0.2	0.2			

(a)

INTENSITY

(c)

DIFFERENCE

(d)

FREQUENCY (cm^{-1})

FREQUENCY (cm^{-1})

DATE

FILMED

4 / 21 / 94

END