

Photolysis of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{NO}]^+$, where M = Mn and Re, in inert ionic matrices Evidence for nitrosyl linkage isomerism

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Abstract

The photochemistry of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{NO}]\text{BF}_4$, where M = Mn and Re, and $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{NO}]\text{PF}_6$ has been examined in frozen ionic matrices, $\text{NEt}_3\text{OctPF}_6$, at ca. 90 K. In each case visible light initiates transformations of the nitrosyl ligand to isonitrosyl and $\eta^2\text{-NO}$ linkage isomers as evidenced by their characteristic IR absorptions. Continued irradiation in the UV results in CO loss as reported by earlier workers. Comparisons with the photochemistry of the Group VI analogues, $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{NO}$, suggest that some features observed in these earlier studies may need to be reinterpreted.

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1. Introduction

Some years ago Hill and co-workers described the photochemistry of $[(\eta^5\text{-C}_5\text{H}_{5-n}\text{Me}_n)\text{Mn}(\text{CO})_2\text{NO}]^+$ cations, where $n = 0, 1,$ and 5 in 1,2-epoxyethylbenzene glass and surface films [1]. In each case, broadband UV photolysis resulted in CO loss as evidenced by a characteristic band at 2132 cm^{-1} attributable to free CO and a shift of the remaining CO and NO bands to lower energy. Extended photolysis resulted in the appearance of additional bands attributed to a variety of CO and NO loss species.

Something of a revolution has occurred in the photochemistry of metal nitrosyl compounds with the discovery by Coppens and coworkers [2] that so-called metastable species resulting from the photolysis of nitroprusside are indeed isonitrosyl and $\eta^2\text{-NO}$ linkage isomers. These three isomeric species are illustrated in Fig. 1. Several additional cases have been confirmed by X-ray photocrystallography [3]. Notably a puzzling intermediate observed by Rest and Crichton in the photochemistry of $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{NO})$ has been shown to be $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\eta^2\text{-NO})$ [4]. We have presented evidence of linkage isomerism in rhenacarborane nitrosyl compounds [5], and have recently observed similar behavior in the Group VI $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{NO}$ and

analogous tris(pyrazoyl)borate derivatives [6]. Evidence is now accumulating to suggest that photochemically induced linkage isomerization is the norm for metal nitrosyl compounds and may be responsible for some observed solution photochemical behavior of these compounds.

To further clarify the behavior of this class of compounds, we have reinvestigated the photochemistry of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{NO}]\text{BF}_4$, $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{NO}]\text{PF}_6$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{NO}]\text{BF}_4$ in an inert tetraalkylammonium PF_6 salt at cryogenic temperatures.¹ The results of this study are reported below.

2. Results

A triethyloctylammonium PF_6 solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{NO}]\text{BF}_4$ was frozen to ca. 90 K in a glass cryostat. The freshly frozen sample was found to have carbonyl bands at 2121 and 2083 cm^{-1} and a nitrosyl band at 1726 cm^{-1} . The sample was photoannealed for 10 min ($\lambda_{\text{irr}} > 600\text{ nm}$) and a comparison of spectra before and after the photoanneal

¹ $\text{NEt}_3\text{Oct PF}_6$ is used in our investigations of ionic materials rather than the more conventional butyl, methylimidazolium PF_6 because we have found several cases in which the latter solvent reacts with photointermediates. Tetraalkylammonium PF_6 salts appear to be ideal “inert” ionic media for these studies.

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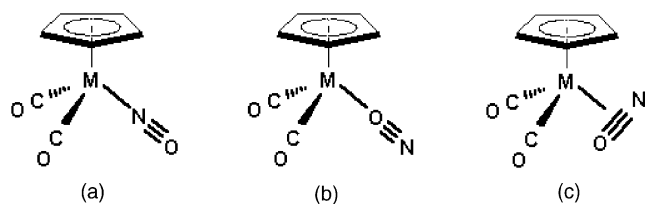


Fig. 1. Nitrosyl linkage isomers: (a) nitrosyl; (b) isonitrosyl; (c) η^2 -NO.

showed no signs of product formation. Continued photolysis (10 min, $\lambda = 450 \pm 35$ nm) resulted in the bleaching of starting material bands, Fig. 1a, and appearance of five new bands at 2101, 2069, 2053, 1726, and 1549 cm^{-1} . There is no evidence for CO loss at this range of wavelengths. The unusual subtraction shape of the nitrosyl band appears to arise from a solvent effect due to the presence of both tetrafluoroborate and hexafluorophosphate anions as it does not appear in the photolysis of the hexafluorophosphate methylcyclopentadienyl derivative. Increasing the photolysis energy on this sample (10 min, $\lambda_{\text{irr}} = 400 \pm 35$ nm) resulted in bleaching of both starting material and the initial product bands and appearance of new bands at 2134, 2069, and 1815 cm^{-1} , Fig. 1b. Subsequent photolysis of this sample (10 min, $330 \text{ nm} < \lambda_{\text{irr}} < 400 \text{ nm}$) resulted in the continued growth of these bands with no new bands observed. Annealing the sample to ca. 150 K results in reversal of the photolysis with reemergence of the starting material bands.

Photolysis of $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{NO}]\text{PF}_6$ under identical conditions displayed similar patterns of behavior.

Irradiation (10 min, $\lambda_{\text{irr}} = 450 \pm 35$ nm) resulted in bleaching of starting material bands and growth of bands at 2100, 2061, 2046, 1716, 1522 and 1506 cm^{-1} . Continued irradiation of this sample at higher energy (10 min, $330 \text{ nm} < \lambda_{\text{irr}} < 400 \text{ nm}$) bleached both starting material and product bands and gave rise to new bands at 2136, 2063, and 1812 cm^{-1} . The observed spectral changes were reproducible on fresh samples (Fig. 2).

Photolysis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{NO}]^+$ was carried out as described for its manganese analogue. $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{NO}]^+$ carbonyl bands were found at 2112 and 2058 cm^{-1} , while the nitrosyl band was at 1707 cm^{-1} . Photolysis (10 min, $\lambda_{\text{irr}} > 450 \text{ nm}$) did not give rise to any observed photoproducts, however, higher energy photolysis on the sample (10 min, $\lambda_{\text{irr}} = 400 \pm 35$ nm) resulted in bleaching of the starting material bands and appearance of six new bands at 2099, 2079, 2038, 2023, 1707, and 1460 cm^{-1} , Fig. 3a. The latter band was buried within CH_2 bending bands of the solvent and thus spectral appearance of this band is noisier than the other bands. Repeated photolyses of several samples confirmed the reproducibility of this band. The source of the small band at 1965 cm^{-1} is unclear. Increasing the photolysis energy (10 min, $330 \text{ nm} < \lambda_{\text{irr}} < 400 \text{ nm}$) results in continued loss of starting material bands, bleaching of the band at 1707 cm^{-1} , and growth of the bands at 2099, 2038 and 1460 cm^{-1} , Fig. 3b. In addition, small bands are observed at 2133 and 1774 cm^{-1} . Upon subsequent photolysis without filters (10 min, $\lambda_{\text{irr}} > 250 \text{ nm}$) the bands at 2133, 2038 and 1774 cm^{-1} grow relative to the other product bands. No new product bands were observed under these conditions.

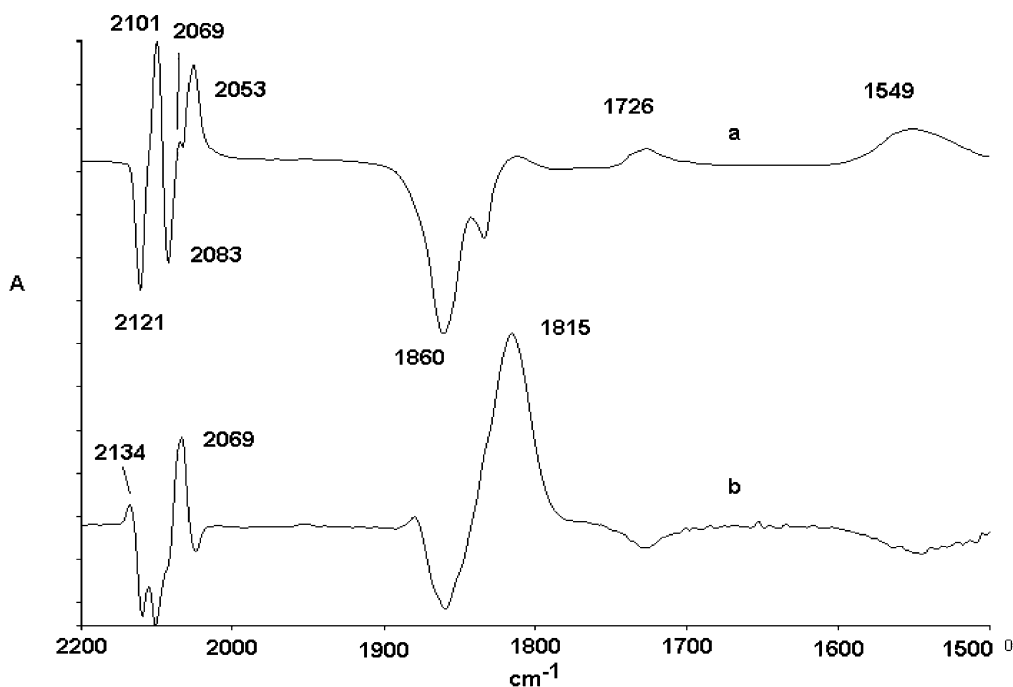


Fig. 2. Difference spectra of the photolysis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{NO}]\text{BF}_4$ in $\text{NEt}_3\text{OctPF}_6$: (a) 10 min, $\lambda_{\text{irr}} = 450 \pm 35$ nm; (b) 10 min, $\lambda_{\text{irr}} = 400 \pm 35$ nm.

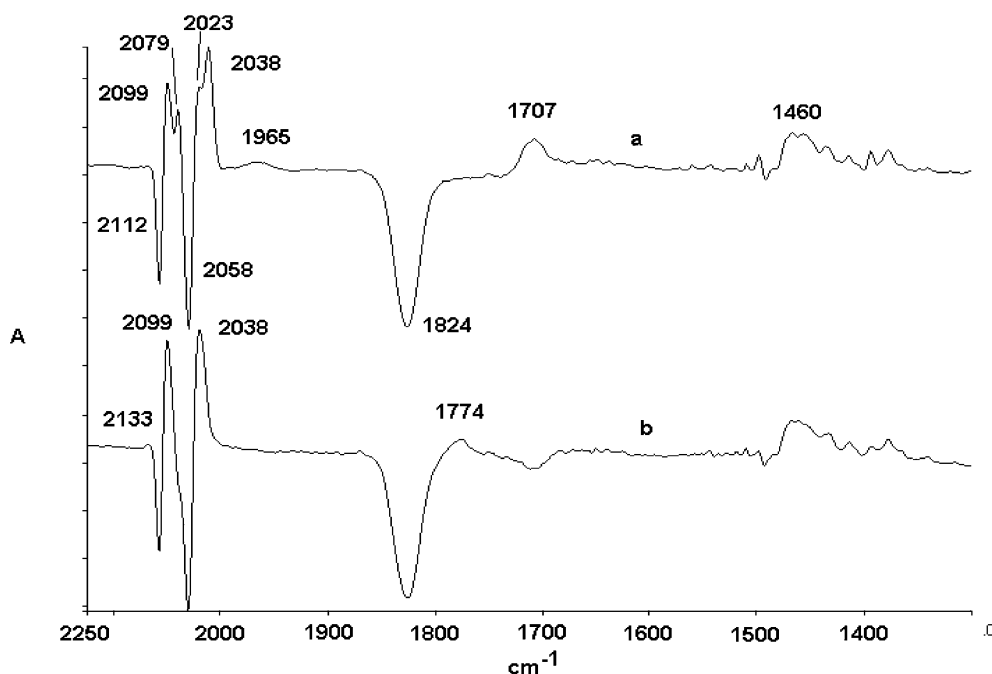


Fig. 3. Difference spectra of the photolysis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{NO}]\text{BF}_4$ in $\text{NEt}_3\text{OctPF}_6$: (a) 10 min, $\lambda_{\text{irr}} = 400 \pm 35$ nm; (b) 10 min, $330 \text{ nm} < \lambda_{\text{irr}} < 400$ nm.

3. Discussion

Both the manganese and rhenium compounds give rise to two new nitrosyl species upon visible photolysis. In the case of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{NO}]^+$ new nitrosyl bands are observed at 1726 and 1549 cm^{-1} , while for its methyl derivative comparable bands are found at 1716, 1522 and 1506 cm^{-1} . These new bands are shifted by 134 and about 320 cm^{-1} , respectively, below the parent nitrosyl band. For each of the two linkage isomeric species we anticipate two terminal carbonyl bands shifted slightly from the positions in the starting material. For both the cyclopentadienyl and methylcyclopentadienyl compounds, only three terminal carbonyl bands (2101, 2069, and 2053 cm^{-1} and 2100, 2061, and 2046 cm^{-1} , respectively) are observed for the two photoproducts, perhaps the result of overlap of the two higher energy bands.

We associate large photochemically induced changes in the stretching frequency of the nitrosyl group ($287\text{--}500 \text{ cm}^{-1}$) with transformation of a terminal nitrosyl to a side-on, $\eta^2\text{-NO}$. For example, in $(\eta^5\text{-C}_5\text{H}_5)\text{Ni}(\text{NO})$ examined by Rest and Crichton, the nitrosyl stretching frequency changes by 440 cm^{-1} in going from the terminal to $\eta^2\text{-NO}$ [4]. In nitroprusside the corresponding change is 287 cm^{-1} [7]. The low energy bands observed here shift by about 320 cm^{-1} and are thus consistent with an assignment to side-on nitrosyl groups.

The nitrosyl photoproduct bands observed at 1726 and 1716 cm^{-1} fall within the very large range often associated with bent nitrosyl groups ($1700\text{--}1400 \text{ cm}^{-1}$). Indeed, a referee has suggested that these bands might be assigned to

bent nitrosyl groups in analogy to the well known examples of linear to bent nitrosyl isomerization in the literature. Regrettably, IR cannot provide definitive assignments, but we feel that an equally strong case can be made for an assignment of these bands to an isonitrosyl linkage isomer.

With one possible exception, those compounds that are observed to exhibit linear to bent nitrosyl behavior are five coordinate species for which the nitrosyl transformation is associated with a structural rearrangement from a trigonal bipyramidal to a square pyramidal geometry [8]. Shifts of nitrosyl stretching frequencies in this class of compounds fall in the range of $70\text{--}105 \text{ cm}^{-1}$ from the parent nitrosyl band. The apparent exception to this rule is $(\eta^3\text{-C}_3\text{H}_5)\text{Ir}(\text{PPh}_3)_2(\text{NO})$ for which the nitrosyl frequency shift is 132 cm^{-1} [9]. Here, the change from linear to bent nitrosyl is presumed to be accompanied by a rotation of the allyl group.

The metals in the Groups VI and VIII $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{NO})$ compounds are generally considered to be octahedrally bound, thus the kinds of structural transformations associated with five coordinate compounds have no analogy here. Further, the changes in nitrosyl stretching frequency (134 cm^{-1}) for the manganese cations examined here are larger than the average of the linear to bent nitrosyl examples. The change in frequency of the nitrosyl group in the isonitrosyl isomer of nitroprusside is 116 cm^{-1} [7]. The comparable shift for the isonitrosyl ligands in iron and ruthenium porphyrin derivatives are in the range of $128\text{--}146 \text{ cm}^{-1}$ [10]. We have observed values in the range of $120\text{--}169 \text{ cm}^{-1}$ for other compounds where we believe isonitrosyl groups might be present. For these reasons we favor assignment of the 1700 cm^{-1} bands to an isonitrosyl linkage isomer.

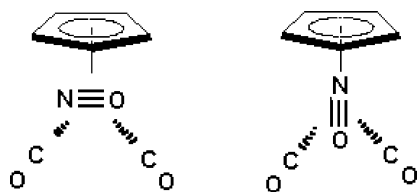


Fig. 4. Proposed rotamers of η^2 -NO linkage isomer.

The observation of two distinct bands for the η^2 -NO group in $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{NO}]^+$ is particularly worth noting. We have observed similar double bands in the isoelectronic Group VI family of compounds and have attributed this to the presence of two nitrosyl rotamers in which the η^2 -NO is parallel or perpendicular to the cyclopentadienyl ring (Fig. 4). Faller and Johnson [11] and Herberhold et al. [12] have proposed analogous rotamers for $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{olefin})$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Cr}(\text{CO})(\text{NO})(\text{alkyne})$ compounds, respectively.

Photolysis of the rhenium compound at the upper end of the visible range results in the appearance of two new nitrosyl bands at 1707 and 1460 cm^{-1} , 117 and 364 cm^{-1} down from the parent nitrosyl band at 1824 cm^{-1} . In the case of rhenium all four expected terminal carbonyl bands are observed for these species.

We have generally observed that carbonyl bands shift to lower energy upon transformation of a terminal nitrosyl to one of its linkage isomers. This pattern requires that the isonitrosyl and η^2 -NO linkage isomers have a net electron withdrawing effect that is slightly less than that of a linear NO. Since linear nitrosyl ligands are generally regarded as having NO^+ character, this observation argues strongly against the nitrosyl linkage isomers being classified as anionic.

Theoretical studies of $[\text{Fe}(\text{CN})_5\text{NO}]^{-2}$ and its ruthenium analogue have been carried out using dft techniques and these results correctly reflect the softening of the NO stretching frequencies on proceeding from nitrosyl to isonitrosyl and η^2 -NO, but provide little detail as to the bonding contributions to these isomeric forms [13]. Earlier studies by Hoffmann on linear and bent nitrosyl bonding [14] and on linear and side-on bonding of diatomics to metal complexes [15] using extended Hückel methods provide a ready visual appreciation for the orbital contributions to the metal to nitrosyl bonding but do not in themselves explain the electronic contributions that cause both the carbonyl and nitrosyl bond stretching frequencies to soften. We are currently exploring these questions with the hope of providing an explanation in future publications.

Both the manganese and rhenium compounds undergo CO loss upon UV photolysis as reported by Hill and co-workers for manganese [1]. The differences in IR band positions ($6\text{--}12\text{ cm}^{-1}$) for the manganese species observed in the present studies relative to those in the earlier work undoubtedly reflect the differences in the tetraalkylammonium PF_6 environment compared with that of 1,2-epoxyethylbenzene

or thin films on CaF_2 . The secondary photolyses reported by the earlier workers were not observed in our tetraalkylammonium PF_6 matrices.

Visible wavelength photolysis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{NO}]^+$, $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{NO}]^+$ and their rhenium analogue give rise to new bands in both the terminal carbonyl and nitrosyl regions that are consistent with the formation of isonitrosyl and η^2 -NO linkage isomers. For these compounds, both linkage isomers form in the same wavelength region unlike the rhenacarborane nitrosyl compounds for which isonitrosyl linkage isomerization occurs at lower energy than η^2 -NO isomer formation. Hill and co-workers observed the formation of several species upon extended photolysis of thin films of $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{NO}]^+$. Among these was the appearance of a pair of bands at 2232 and 1929 cm^{-1} attributed to “free” NO^+ and “ $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})$ ”, respectively. No reference was cited for the assignment of the nitrosonium ion to the band at 2232 cm^{-1} although gas phase NO^+ has been reported to have a vibrational band at about 2289 cm^{-1} [16]. By comparison, solutions of NOBF_4 in acetonitrile and butyl, methylimidazolium PF_6 have bands at 1872 and 1878 cm^{-1} , respectively, attributable to the nitrosonium ion. We have not been able to reproduce these bands, but an assignment to an NO^+ seems unlikely.

The results of these studies and others from this and other laboratories suggests that photochemical linkage isomerism is a common, if not universal, property of nitrosyl ligands. To what extent these linkage isomers play a role in the observed chemistry of these compounds is presently under investigation.

4. Experimental

$[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{NO}]^+$ and its rhenium analogue were dissolved in molten $\text{NEt}_3\text{OctPF}_6$ at about 80°C and resulting ionic mixture was pressed, with heating, between two CaF_2 windows to produce a thin film. Photolyses were carried out using a liquid nitrogen cooled glass cryostat designed by Rest as previously described [17]. Nominal sample temperatures are ca. 90 K . The output from a 350 W high pressure mercury lamp was passed through a 40 mm quartz windowed water filter. Irradiation wavelengths were controlled using a series of optical filters bandpass filters. IR spectra were recorded on a Perkin-Elmer Spectrum 1000 Infrared Spectrometer with a resolution of 2 cm^{-1} . $[(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{NO}]\text{BF}_4$ [18] $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2\text{NO}]\text{PF}_6$ [19] and $[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})_2\text{NO}]\text{BF}_4$ [20] were prepared by literature methods.

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