



*Dedicated to the memory of
our dear friend and colleague
Prof. Ioan Silaghi-Dumitrescu*

MATRIX PHOTOCHEMISTRY AND DFT INVESTIGATION OF ANIONIC (η^5 -C₅H₅)Cr(CN)₃. INDIRECT OBSERVATION OF 13- S=3/2 Cr(III)

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Matrix isolation Fourier transform infrared spectroscopy (FTIR) in polyvinyl chloride film (PVC) at 90 K combined with density functional theory calculations (DFT) has been used to study the photochemical reactivity of 15-electron (S=3/2) [PPh₄][CpCr(CN)₃], Cp = η^5 -C₅H₅. Photolysis (450 > λ > 280 nm) results in loss of CN⁻. DFT calculations support the generation of neutral 13-electron S=3/2 CpCr(CN)₂. Photolysis of [PPh₄][CpCr(CN)₃] in CH₂Cl₂ under CO atmosphere and in the presence of excess phosphine afforded only recovery of the parent compound.

INTRODUCTION

Matrix isolation FTIR has been an essential tool for characterizing intermediates in the photochemical reactions of organometallic compounds. However, despite numerous solution studies¹⁻⁷, surprisingly few matrix photochemistry experiments have been performed to investigate complexes of the cyanide ligand^{8,9}. As part of our general investigation of linkage isomerism in ambidentate ligands, our attention has recently been given to this class of compounds. Here we present the matrix photochemistry of [PPh₄][CpCr(CN)₃], Cp = η^5 -C₅H₅ as well as density functional theory (DFT) calculations of its linkage isomers and CN⁻ loss products.

[PPh₄][CpCr(CN)₃], like other cyclopentadienyl compounds of Cr(III), is a 15-electron species with a spin quartet ground state¹⁰⁻¹³. Mattamana and Poli's investigation of this compound yielded the first 17-electron half-sandwich complexes of Cr(III) stable at room temperature, taking the form

CpCr(CN)₂L₂, (L = PMe₃, PMe₂Ph, dmpe, dmpm).¹⁴ Though these species were not isolable, the parent compound's reactivity seemed to make it a reasonable candidate to begin our investigation of the photochemistry of cyanide complexes. Remarkably, [PPh₄][CpCr(CN)₃] was found to have an extremely small extinction coefficient in the cyanide stretching region of the infrared, making the task of distinguishing between linkage isomers unlikely using FTIR. Nevertheless, matrix photochemistry experiments were conducted to monitor for CN⁻ loss.

EXPERIMENTAL

[PPh₄][CpCr(CN)₃] was prepared by literature methods¹⁴. The apparatus and methods for matrix photochemistry have been reported elsewhere¹⁵. Infrared spectra were recorded on a Perkin Elmer Spectrum 1000 FTIR Spectrometer. UV-Vis spectra were recorded on an Ocean Optics USB2000 fiber optic spectrometer. All density functional calculations were performed in NWChem¹⁶ and MO visualizations done in ECCE.¹⁷ A valence triple- ζ basis set containing two sets of

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polarization functions and augmented by a diffuse function (VTZ2PD) was employed on all atoms¹⁸⁻²⁰ except chromium for which the LANL2TZ+ ECP²¹ was used. The quadrature for the numerical integration grid used an Euler-MacLaurin scheme with a modified Mura- Knowles transformation for the radial components and a Lebedev scheme for the angular components. This had a total energy target accuracy of 1×10^{-7} . For all calculations B88P86, a pure GGA combining Becke's 1988 exchange functional²² with Perdew's 1986 correlation functional²³ was used. No symmetry constraints were applied when performing calculations. All geometries were confirmed as local minima on the potential energy surface as indicated by the lack of imaginary frequencies in the frequency calculation. Spin contamination was monitored by the expectation value $\langle S^2 \rangle$, which in all cases deviated less than 5% from ideal values.

RESULTS

(a) Matrix Photochemistry. Irradiation of the parent compound ($450 > \lambda > 280$ nm) at 90 K resulted in bleaching of the parent compound at 2116 cm^{-1} and 2070 cm^{-1} for its ^{13}CN isotopomer as well as liberation of free CN^- at 2077 cm^{-1} and 2031 cm^{-1} for the ^{13}CN isotopomer. Back photolysis with 550 nm resulted in complete reversal of the CN^- loss (Fig. 2).

(b) Density. Functional. Theory.

Table 1
Isomers $[\text{CpCr}(\text{CN})_3]^-$

Compound	Multiplicity	ΔE (kcal mol^{-1})	$\nu(\text{CN}) \text{ cm}^{-1}$ (KM/mole)
$[\text{CpCr}(\text{CN})_3]^-$	$S = 3/2$	0	2093 (0.42), 2095 (0.07), 2096 (0.07)
$[\text{CpCr}(\text{CN})_3]^-$	$S = 1/2$	29.09	2067 (38.72), 2079 (24.26), 2093 (0.82)
$[\text{CpCr}(\text{CN})_2(\text{NC})]^-$	$S = 3/2$	6.92	2025 (176.48), 2101 (0.143)
$[\text{CpCr}(\text{CN})_2(\text{NC})]^-$	$S = 1/2$	23.81	2008 (178.31), 2080 (0.27)
$[\text{CpCr}(\text{CN})(\text{NC})_2]^-$	$S = 3/2$	14.07	2029 (215.54), 2031 (155.39), 2106 (0.02)
$[\text{CpCr}(\text{CN})(\text{NC})_2]^-$	$S = 1/2$	31.12	2009 (216.35), 2017 (137.03), 2093 (0.57)
$[\text{CpCr}(\text{NC})_3]^-$	$S = 3/2$	21.16	2033 (206.32), 2035 (208.58), 2037 (132.54)
$[\text{CpCr}(\text{NC})_3]^-$	$S = 1/2$	53.7	2010 (252.11), 2030 (106.81), 2033 (86.33)

Table 2
Isomers of $\text{CpCr}(\text{CN})_2$

Compound	Multiplicity	ΔE (kcal mol^{-1})	$\nu(\text{CN}) \text{ cm}^{-1}$ (KM/mole)
$\text{CpCr}(\text{CN})_2$	$S = 3/2$	0	2105 (67.58), 2107 (70.78)
$\text{CpCr}(\text{CN})_2$	$S = 1/2$	29.92	2071 (19.61), 2072 (20.82)
$\text{CpCr}(\text{CN})(\text{NC})$	$S = 3/2$	3.31	1985 (498.66), 2114 (55.04)
$\text{CpCr}(\text{CN})(\text{NC})$	$S = 1/2$	23.54	1964 (467.59), 2083 (9.54)
$\text{CpCr}(\text{NC})_2$	$S = 3/2$	88.58	2018 (5.80), 2021 (3.98)
$\text{CpCr}(\text{NC})_2$	$S = 1/2$	29.83	1963 (500.76), 1977 (245.36)

Table 3

Selected Bond Lengths and Angles for $S = 3/2$ CpCr(CN)

Cr-CN	1.984	Cr-CNT	1.992
NC-Cr-CN	100.4	NC-Cr-CNT	130.1

DISCUSSION

Photolysis of $[\text{PPh}_4][\text{CpCr}(\text{CN})_3]$ initiated with wavelengths of light corresponding to the first CT band at 420 nm (Fig. 1) and higher results in the liberation of the cyanide anion. Back photolysis with 550 nm light results in recapture of the free CN^- . Unfortunately, attempts to characterize this compound by EPR in organic glass matrices at 77 K failed; suggesting that the photoproduct, like the parent compound and some other low symmetry spin quartet half-sandwich complexes of Cr(III)^{14, 24-25} is EPR silent. Further attempts to support the formation of $\text{CpCr}(\text{CN})_2$ by photolyzing the parent compound in the presence of 1 equivalent of PPh_3 or under and an atmosphere of CO in an effort to observe $\text{CpCr}(\text{CN})_2\text{PPh}_3$ or $\text{CpCr}(\text{CN})_2(\text{CO})$ spectroscopically were unsuccessful.

Attempts to unambiguously assign the transitions in the UV-Vis with time-dependent DFT were unfruitful. Calculations using both

random phase and Tamm-Dancoff approximations gave results with significant spin contamination; a common result for calculations of open-shell molecules. The Kohn-Sham frontier orbitals of $[\text{CpCr}(\text{CN})_3]^-$ are presented in Fig. 3. The singly occupied molecular orbitals are predominately metal-d in character with a small amount of $\text{CN}^- \pi$ -backbonding. The lowest unoccupied molecular orbitals are predominately metal-d CN^- anti-bonding in character.

Calculated relative energies and infrared absorptions for isomers for $[\text{CpCr}(\text{CN})_3]^-$ and $\text{CpCr}(\text{CN})_2$ are presented in Tables 1 and 2. For isomers of $[\text{CpCr}(\text{CN})_3]^-$ only those with a N bound cyanide have an appreciable infrared absorption in the CN stretching region. $[\text{CpCr}(\text{CN})_2(\text{NC})]^-$ lies just 6.92 kcal \times mol⁻¹ above the parent compound, however, no product assignable to this species was seen with photolysis by $\lambda > 450$ nm.

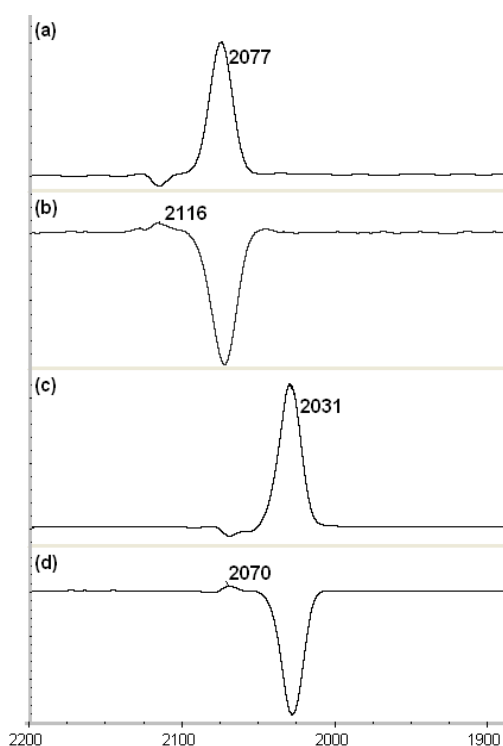


Fig. 2 – Infrared spectra of $[\text{PPh}_4][\text{CpCr}(\text{CN})_3]$ and ^{13}C isotopomer (a) and (c) after $450 > \lambda > 280$ nm irradiation. (b) and (d) after 550 nm back photolysis.

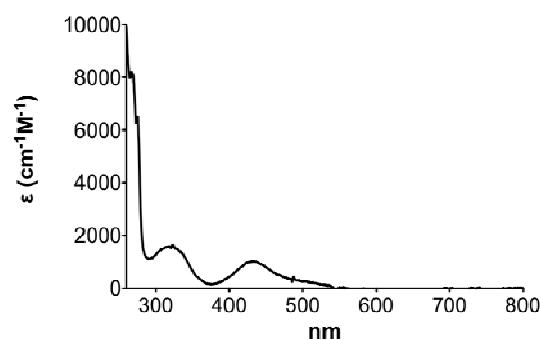


Fig. 1 – UV-Vis spectra of $[\text{PPh}_4][\text{CpCr}(\text{CN})_3]$ in CH_2Cl_2 .

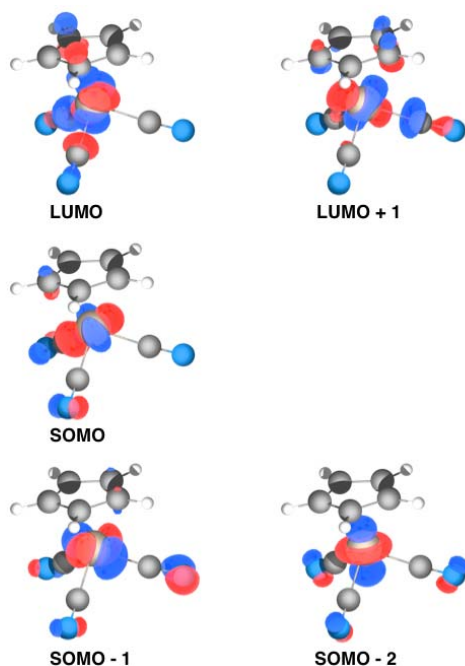


Fig. 3 – Kohn-Sham orbitals of $[\text{CpCr}(\text{CN})_3]$.

Not unlike the isomers of $[\text{CpCr}(\text{CN})_3]$, only the isomers of $\text{CpCr}(\text{CN})_2$ which have a N bound cyanide have strong absorbances in the CN stretching region of the infrared. $S = \frac{3}{2}$ $\text{CpCr}(\text{CN})_2$ is calculated to be the lowest energy isomer with $\text{CpCr}(\text{CN})(\text{NC})$ lying just $3.31 \text{ kcal} \times \text{mol}^{-1}$ above. The energy cost of spin-pairing and further isomerization of the cyanide ligands greatly increase the relative energy to $\text{CpCr}(\text{CN})_2$. Relevant bond lengths and angles of the lowest energy CN^- loss product are presented in Table 3. Optimizations converged upon a Cs structure in which both remaining cyanide ligands are bent slightly away from the vacant coordination site.

Though coordinatively unsaturated complexes of Cr(III) are rare,²⁶ 13-electron pentacoordinate compounds of Cr(III) are not unknown. 13-electron intermediates are thought to play a vital role in Cr(III) catalysis,^{12, 27-28} and in elegant work Theopold and coworkers were able to structurally characterize such a compound.²⁹ However, $\text{CpCr}(\text{CN})_2$ is a unique addition to this club as the cyanide ligand is both sterically undemanding and a high-field ligand, two characteristics not shared with those of other 13-electron Cr(III) complexes.

CONCLUSIONS

Matrix isolation FTIR and DFT calculations have been used to demonstrate the reversible photochemical loss of CN^- from $[\text{PPh}_4][\text{CpCr}(\text{CN})_3]$

in a PVC matrix. $\text{CpCr}(\text{CN})_2$ is a unique 13 electron pentacoordinate spin-quartet complex of Cr(III).

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