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The photochemistry of $Mo(CNPh)_6$: dissociative photosubstitution and evidence for ‘hot’ electron transfer

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Contents

Abstract

The photosubstitution reactivity of $Mo(CNPh)_6$ was investigated by studying the effects of nucleophile and nucleophile concentration. Substitution quantum yields were identical for pyridine and PPh_3 as nucleophiles. Between 0.1 and 4×10^{-4} M pyridine, there was no change in quantum yield. These observations suggest that photosubstitution in $Mo(CNPh)_6$ is dissociative in character, not associative as previously thought. Photoinduced electron transfer from $Mo(CNPh)_6$ to chloroform, producing $[Mo(CNPh)_6Cl]^+$, was also measured. While photosubstitution is wavelength independent, photoinduced electron transfer quantum yields are wavelength dependent. The electron transfer quantum yield is highest at 313 nm (0.77) and decreases to a constant value of 0.28 at 436 nm. It is proposed that this evidence supports a ‘hot’ electron transfer process, where electron transfer occurs prior to vibrational relaxation into the metal-to-ligand charge transfer (MLCT) manifold.

Keywords: Photosubstitution reactivity; ‘Hot’ electron transfer; $Mo(CNPh)_6$

1. Introduction

The photoreactions of organometallic complexes containing low-lying metal-to-ligand charge transfer (MLCT) states is a topic of major interest up to the moment in the Stufken laboratories [1]. The arylisonitrile complexes $M(CNAr)_6$ (M = Cr, Mo, W; Ar = aryl group) offer a unique opportunity to study the substitutional reactivity of MLCT states because of their low-lying, intense MLCT absorptions and the high energy of their ligand field states. We recently reported a complete study of the wavelength dependence of the photochemistry of $Cr(CNPh)_6$ (CNPh = phenylisocyanide) [2].

The first work on $M(CNAr)_6$ photochemistry and spectroscopy was performed by Mann and Gray in the 1970s [3–5]. They observed two basic photochemical pathways in these compounds: photosubstitution in the presence of nucleophiles, and photoinduced electron transfer in chlorinated solvents. Photosubstitution

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quantum yields, ϕ_{sub}, were measured in $M(CNPh)_6$ and the analogs $M(CNIph)_6$ (CNIph = 2,6-diisopropylphenylisocyanide). The CNIph ligand was used to create a sterically protected metal centre in the complexes, which would hinder any associative substitution mechanism. On comparing ϕ_{sub} for $M(CNPh)_6$ and $M(CNIph)_6$, it was observed that for M = Cr, ϕ_{sub} remained constant but for M = Mo, W, ϕ_{sub} was lower for the $M(CNIph)_6$ compounds. It was thus concluded that the photosubstitution mechanism is dissociative for $Cr(CNAr)_6$ compounds and associative for $Mo(CNAr)_6$ and $W(CNAr)_6$.

Mann and Gray also showed that in halogenated solvents, excitation into the MLCT absoptions results in electron transfer products. $Cr(CNIph)_6$ produces $[Cr(CNIph)_6]^+$ when irradiated in chloroform. Irradiation of $Cr(CNPh)_6$ in chloroform leads to Cr(II) products. When $Mo(CNPh)_6$ is irradiated in chloroform, the seven-coordinate Mo(II) complex $[Mo(CNPh)_6Cl]^+$ is formed via a radical mediated pathway with a quantum yield of 0.11 at 436 nm.

Emission properties of $M(CNPh)_6$ compounds show further differences between the Cr and Mo, W analogs. Unlike the Cr analogue, $Mo(CNPh)_6$ has an emissive state at room temperature. The emission is not substantially Stokes shifted (i.e. there is significant overlap of the lowest energy MLCT absorption and the emission maximum at 17 900 cm^{-1}). This is suggestive of a thermally equilibrated excited state. At 77 K, the quantum yield of emission is 0.78. The emission lifetimes are 21 ns (298 K) and 23 μs (77 K) [3].

The dissociation of a CNPh ligand in $Cr(CNPh)_6$ is ultrafast, occurring in less than 1 ps [6]. Resonance Raman data on $Cr(CNPh)_6$ indicate very large relative displacements of the δ(Cr–C–N) and δ(C–Cr–C) bending modes on excitation into the low energy tail of the broad MLCT absorption band [7]. Such excited state distortion could explain the mechanism of ultrafast ligand dissociation in $Cr(CNPh)_6$—electronic excitation is vibronically coupled to modes that lead to bond cleavage.

Detailed investigations of $Cr(CNPh)_6$ photochemistry and wavelength dependence have now been reported. In this paper, we report a more thorough investigation of photosubstitution in $Mo(CNPh)_6$, including wavelength dependence. We also report the wavelength dependence of photoinduced electron transfer, which provides direct evidence for an electron transfer process competing with vibrational relaxation.

2. Experimental

2.1. Materials

All procedures involving molybdenum complexes were performed under nitrogen using Schlenk techniques. Benzene and $C_6H_5CH_3$ were distilled from sodium benzophenone ketyl. Chloroform was distilled from CaH_2 in the dark immediately prior to a reaction. Pyridine was distilled from CaH_2. Triphenylphosphine was obtained from Aldrich. Phenylisocyanide was prepared according to Weber et al. [8]. $Mo_2(CH_3CO_2)_4$ was prepared from $Mo(CO)_6$ according to Brignole and Cotton [9].

$Mo(CNPh)_6$ was synthesized according to Mann et al. [4] by the addition of phenylisocyanide (10 ml) in 20 ml of CH_3OH to a slurry of $Mo_2(CH_3CO_2)_4$ (1.0 g) in 40 ml of CH_3OH. The mixture was stirred for 1 h in the dark. The red precipitate was filtered and washed with CH_3OH and then recrystallized from $C_6H_5CH_3$. Crystals were washed with $C_6H_5CH_3$ (2 × 5 ml) to remove traces of phenylisocyanide. Yield: 0.48 g (86% based on the disproportionation reaction). Purity was established by comparison to the published UV–vis spectra.

2.2. Quantum yield measurements

UV–vis spectra were measured on an HP-8452A photodiode array spectrophotometer. Irradiations were performed in a quartz circular cell with a fused joint connected to a teflon stopcock and a side arm with bulb for freeze/pump/thaw cycles. Samples were subjected to five freeze/pump/thaw cycles prior to irradiation. The light source was a PRA model ALH 215 xenon medium pressure arc lamp (150 W) coupled with the appropriate interference filter. Samples were stirred during irradiation with a magnetic stir bar. Ferrioxalate [10] and fulgide [11] actinometry were used for light intensity measurements. Quantum yields were always determined using data from the first 10% of the reaction in order to avoid secondary photolysis.

Table 1
$Mo(CNPh)_6$ photosubstitution quantum yield dependence on pyridine concentration in benzene

[py] (M)	Quantum yield (±0.01)
0.10	0.18
1.0×10^{-2}	0.17
6.0×10^{-3}	0.16
2.0×10^{-3}	0.17
4.0×10^{-4}	0.17

2.3. Nanosecond flash photolysis

Nanosecond flash photolysis experiments were performed at the University of Victoria using a system described in the literature [12].

3. Results and discussion

The nucleophile dependence of photosubstitution in $Mo(CNPh)_6$ was determined in order to test the putative associative mechanism. Quantum yields were determined in benzene with pyridine and triphenylphosphine as nucleophiles. At 436 nm, the quantum yield of photosubstitution (ϕ_{sub}) was 0.17 ± 0.01 for both pyridine and PPh_3 (0.01 M). The absence of a nucleophile dependence is a strong evidence against an associative mechanism.

The dependence of ϕ_{sub} on nucleophile concentration was also determined (Table 1). Over three orders of magnitude in pyridine concentration there is no change in ϕ_{sub}. The excited state has a lifetime of 21 ns at 298 K [3,5]. Thus, if substitution on the excited state was bimolecular, nucleophile concentration effects would be observed at nucleophile concentrations on the order of 5×10^{-3} M (assuming a diffusion controlled rate constant $k_{diff} = 1.0 \times 10^{10}$ M^{-1} s^{-1} in benzene). This is not the case, so the nucleophile must be reacting with solvated species of the type '$Mo(CNPh)_5S$' produced as the primary product of photodissociation.

The wavelength dependence of ϕ_{sub} in neat pyridine was determined (Table 2). Within experimental error, there is no wavelength dependence. These results confirm the previously reported substitution quantum yield at 313 nm, but suggest that the previous 436 nm yield (0.055) [3] is incorrect.

A wavelength independent quantum yield is good evidence that the reaction is occurring from a thermally equilibrated excited state where 'memory' of the excess excitation energy is lost through vibrational relaxation prior to the process(es) leading to substitution. This agrees with the emission data. For substitution to occur from a thermally relaxed MLCT excited state with negligible antibonding character, population of a higher lying dissociative state is required.

Table 2
Wavelength dependence of photosubstitution on $Mo(CNPh)_6$ in neat pyridine

Wavelength (nm)	Quantum yield (±0.01)
313	0.11
365	0.11
436	0.12
488	0.12

Preliminary flash photolysis experiments were performed on $Mo(CNPh)_6$ in pyridine to further explore the possibility of an associative photosubstitution mechanism. It was observed that the $Mo(CNPh)_5py$ product absorption at 550 nm was completely formed within 20 ns, 532 nm flash. By setting the monitoring wavelength to the isosbestic point of the reaction (506 nm), the presence of any intermediate different from $Mo(CNPh)_6$ and the product $Mo(CNPh)_5py$ (e.g. a seven-coordinate intermediate) would be detected. In this experiment, no deviation from zero absorption change was observed, suggesting that there is no such intermediate on this timescale. Considering the 21 ns fluorescence lifetime, these observations are not surprising since primary photochemical processes must occur prior to excited state decay. However, a meta-stable intermediate with a sub-microsecond lifetime is not observed in this system where the solvent is also the final ligand.

On the basis of the interpretation of wavelength dependence above, the photosubstitution occurs via the population of a reactive LF state from a thermally relaxed MLCT state, it was hypothesized that the quantum yield for the photoinduced electron transfer reaction in chloroform should also be wavelength independent:

$$Mo(CNPh)_6 \xrightarrow{h\nu,\ CHCl_3} [Mo(CNPh)_6Cl]^+$$

The dependence of ϕ_{et} on excitation energy is shown in Fig. 1. There are two regions of wavelength dependence: at high excitation energies (corresponding to 313 and 365 nm) ϕ_{et} decreases with decreasing excitation energy; at low excitation energies (corresponding to 436 and 488 nm) ϕ_{et} has approached a limit and is no longer dependent on excitation energy.

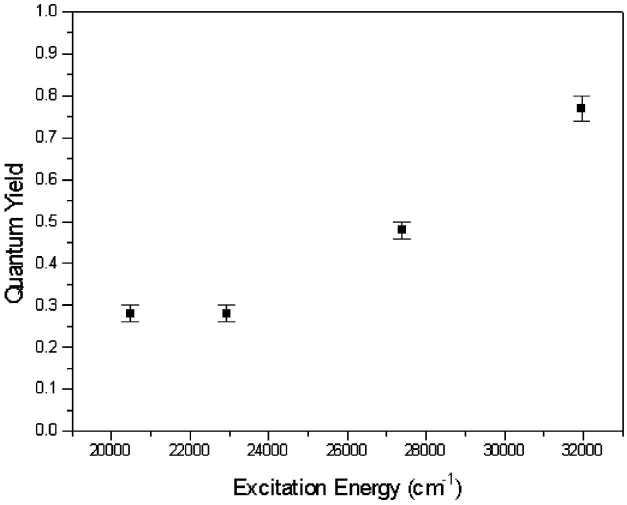
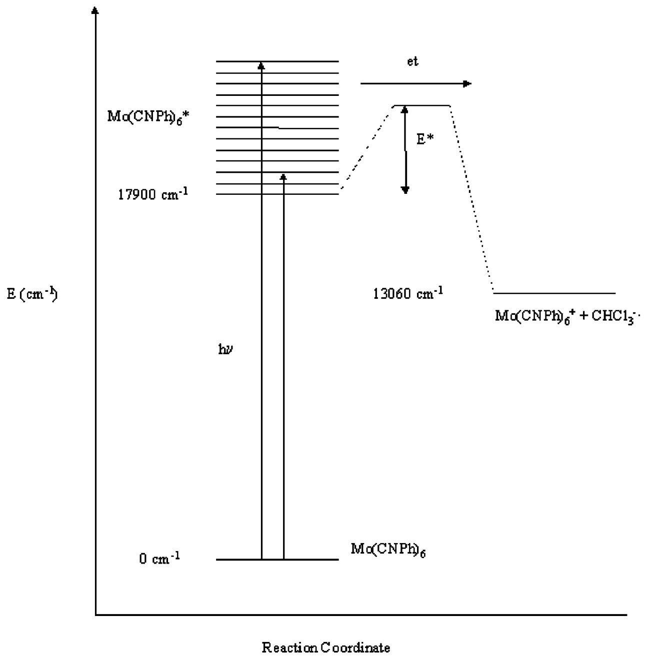


Fig. 1. Excitation energy dependence of electron transfer quantum yield for $Mo(CNPh)_6$ in chloroform. Error bars represent the standard deviation.



Scheme 1.

Scheme 1 provides a framework for understanding this result. First, the lowest lying MLCT state lies 17 900 cm^{-1} above the zeroth vibrational level of the ground state [3]. The MLCT manifold of states extends much higher, to ca. 30 000 cm^{-1} (a $d\pi \rightarrow \pi_v^*$ absorption at 26 500 cm^{-1} and a $d\pi \rightarrow \pi_h^*$ absorption at 31 950 cm^{-1} are the two highest energy MLCT absorptions) [13]. Thus, all irradiation wavelengths directly populate MLCT states.

The half wave potential $E_{1/2}$ for oxidation of $Mo(CNPh)_6$ is −0.19 V (vs. SCE) [14]. The $E_{1/2}$ for one electron reduction of chloroform is −1.67 V (vs. SCE) [15]. From these thermodynamic quantities it is possible to calculate the relative energy of the primary electron transfer products $Mo(CNPh)_6^+$ + $Mo(CNPh)_6^+ + CHCl^{-\bullet}$. Using the equation $\Delta G = -nFE$ (F, Faradays's constant, n, number of moles of electrons transferred) and converting to wavenumbers, the products are 13 060 cm^{-1} above the ground state of $Mo(CNPh)_6$.

We assume that this electron transfer reaction is in the 'normal region'—where there is a classical activation energy requirement for the electron transfer to take place. If the excitation energy contained in a photon results in population of MLCT states that lie below the activation energy for electron transfer (E^*), the system may undergo vibrational relaxation prior to electron transfer to the solvent (chloroform)—thereby losing 'memory' of excess excitation energy and leading to wavelength independence. Alternatively, if the excitation energy is sufficient to populate MLCT states at or above the energy barrier to electron transfer (i.e. 17 900 $\text{cm}^{-1} + E^*$), an excitation energy dependence may result: the greater the excess energy, the higher the probability that the system will undergo electron transfer prior to vibrational relaxation and trapping in the lower levels of the MLCT manifold, leading to a larger ϕ_{et}. In other words, at shorter wavelengths, 'hot' electon transfer is possible.

It is possible that the increase in electron transfer yield in the UV region is due to a CTTS absorption. This is difficult to ascertain because no additional electronic absorptions are observed on going from aromatic solvents to chloroform. It is possible, however, that a CTTS absorption in obscured by the very strongly absorbing MLCT transitions. The electric and magnetic circular dichroism spectra of $Mo(CNPh)_6$ could provide an answer to this question.

This apparent 'hot' electron transfer is of fundamental and practical interest. Hot electron transfer is potentially important in solar energy conversion and photocatalysis, where it is important to maximize the conversion of photon energy into a chemical process (typically an electron transfer). Examples of heterogeneous 'hot' electron transfer have been suggested and are a current research area that can be informed by homogeneous examples. These experiments on $Mo(CNPh)_6$ appear to provide the first direct homogeneous example of the enhancement of electron transfer efficiency that can result from the presence of a 'hot' electron transfer process. In this case, ϕ_{et} almost triples in magnitude between 22 950 and 31 950 cm^{-1} (Fig. 1).

In recent work on $W(CO)_4$phen by Lindsay et al. [16] it was found that 'hot' electron transfer was competing with photosubstitution. In tetrachloroethylene (TCE), a solvent capable of accepting an electron, the quantum yield for photosubstitution increased with decreasing excitation energy (i.e. increasing wavelength). This contrasts to the behaviour in solvents such as pyridine and toluene—solvents that have large reduction potentials which energetically hinders any electron transfer to solvent. In pyridine and toluene, the substitution quantum yields were observed to be wavelength independent for direct excitations into MLCT states. This wavelength independence in the MLCT region has also been observed in a larger study on $M(CO)_4$phen compounds that also used toluene as a solvent [17]. The different wavelength dependence in TCE could arise if photoinduced electron transfer to the solvent were occurring in competition with substitution. As the 'hot' electron transfer increased in efficiency at higher excitation energies, the number of successful substitutions would decrease. Note that time resolved data on $W(CO)_4$phen gave evidence for bimolecular photoinduced electron transfer faster than 30 ps, which is on the time scale of vibrational relaxation and suggests that such a competition between electron transfer and substitution is reasonable. The $Mo(CNPh)_6$ results presented here directly confirm that electron transfer can be enhanced at higher excitation energies and support the explanation of $W(CO)_4$phen reactivity.

The differences in photochemistry between $Cr(CNPh)_6$ and $Mo(CNPh)_6$ are non-trivial. In $Cr(CNPh)_6$, photosubstitution occurs in < 1 ps, quantum yields are higher than in $Mo(CNPh)_6$ and ϕ_{sub} increases with increasing excitation energy, a common feature among ultrafast photodissociations. These features are consistent with relatively lower lying LF states in the chromium compound—where internal conversion from MLCT to LF states is facile. In $Mo(CNPh)_6$, population of higher lying LF states is not as favourable and the MLCT → LF internal conversion is slower. Thus, $Mo(CNPh)_6$ exhibits features of 'thexi' state photochemistry: an emission that shows negligible Stokes shift and a wavelength independent photosubstitution quantum yield.

The quantum yields for electron transfer found in this work are significantly higher than previously reported. It should be noted that at 436 nm ϕ_{et} in the tungsten complex $W(CNPh)_6$ was reported as 0.28, the same as found here for $Mo(CNPh)_6$ at this wavelength. The difference in $Mo(CNPh)_6$ results may have arisen from the method of monitoring the progress of reaction. In this work, ϕ_{et} was determined by monitoring the decrease in $Mo(CNPh)_6$ absorption at 520 nm. Mann monitored the small absorption increase in the 600 nm region. Small absorbance changes present a serious challenge to accuracy. It is also possible that small quantities of quenching impurities were present in samples used in the previous work. We found that the quantum yield measurements were highly sensitive to the purity of the chloroform that was used.

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