

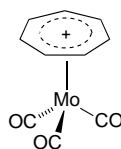
# Excited state properties of the (tropylium)molybdenum tricarbonyl cation

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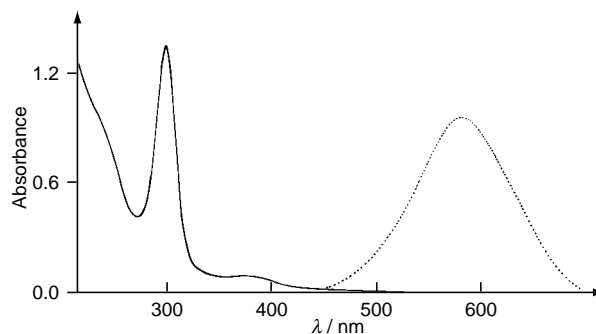
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The electronic spectrum of  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}^0(\text{CO})_3]^+$  shows its longest-wavelength absorption at  $\lambda_{\text{max}} = 379 \text{ nm}$  which is assigned to a  $\text{Mo}^0 \rightarrow \eta\text{-C}_7\text{H}_7^+$  MLCT transition; the  $^3\text{MLCT}$  excited state is luminescent at room temperature; solid  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}^0(\text{CO})_3]\text{PF}_6$  as well as solutions of the complex in MeCN display this emission at  $\lambda_{\text{max}} \text{ ca. } 580 \text{ nm}$ ; the MLCT state is also reactive; in EtOH solutions  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}^0(\text{CO})_3]^+$  is reduced to  $[(\eta\text{-C}_7\text{H}_8)\text{Mo}^0(\text{CO})_3]$  with  $\phi = 0.18$  at  $\lambda_{\text{irr}} = 366 \text{ nm}$ .

An important family of luminescent transition metal compounds comprises polypyridyl complexes such as  $[\text{Ru}^{\text{II}}(\text{bipy})_3]^{2+}$ <sup>1,2</sup> and  $[\text{Re}^{\text{I}}(\text{bipy})(\text{CO})_3\text{Cl}]$ .<sup>3-5</sup> These emitters are characterized by a reducing  $d^6$  metal ion of the second or third transition series and heteroaromatic ligands which provide low-energy empty  $\pi^*$  orbitals. The emission originates from the lowest energy metal-to-ligand charge transfer (MLCT) triplet excited state. An analogous behavior may be observed for organometallic complexes which contain aromatic molecules or ions such as benzene or cyclopentadienyl anion as  $6\pi$ -electron ligands. Unfortunately, the metal  $\rightarrow \pi^*$  (aromatic hydrocarbon) MLCT states of such complexes are apparently located above the lowest energy ligand-field (LF) excited states. Accordingly, these compounds do not emit under ambient conditions, but undergo photosubstitution.<sup>3</sup> However, an emission could occur, if by a suitable choice of the aromatic ligand, the MLCT state is pushed below the LF states. In contrast to  $\text{C}_5\text{H}_5^-$  and  $\text{C}_6\text{H}_6$ , the tropylium cation is a strong acceptor.<sup>6,7</sup> The electronic spectra of ion pairs consisting of  $\text{C}_7\text{H}_7^+$  and donor anions such as  $\text{I}^-$  show characteristic long-wavelength outer sphere CT absorptions.<sup>7-9</sup> It follows that the tropylium cation should be an appropriate acceptor ligand in order to observe a low-energy and hence emitting MLCT state. We explored this possibility and selected the cation  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}^0(\text{CO})_3]^+$ <sup>10-13</sup> for the present study. This complex is easily accessible from  $[(\eta\text{-C}_7\text{H}_8)\text{Mo}^0(\text{CO})_3]$ <sup>11,14</sup> which is commercially available (Aldrich).



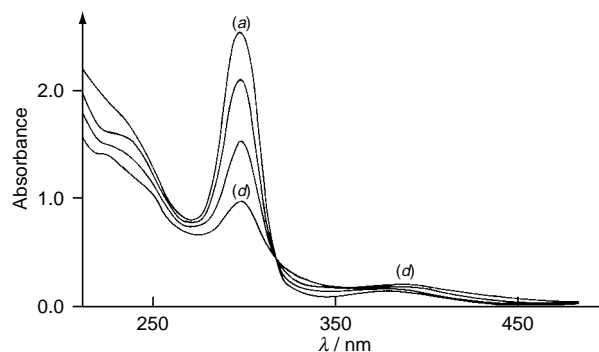
The electronic spectrum of  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$  in EtOH (Fig. 1) shows absorptions at  $\lambda_{\text{max}} = 379 \text{ nm}$  ( $\epsilon/\text{dm}^3 \text{ mol}^{-1}$  1200), 298 (23 800), 236 (sh, 15 800). The energy of the long-wavelength bands is scarcely dependent on the solvent polarity. Solid  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]\text{PF}_6$  shows a yellow emission at  $\lambda_{\text{max}} = 580 \text{ nm}$  at room temperature. In solution this luminescence is slightly shifted (Fig. 1) and appears at  $\lambda_{\text{max}} = 578 \text{ nm}$ . The excitation spectrum of  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$  matches essentially the absorption spectrum. This emission intensity is rather low in solution ( $\phi \text{ ca. } 10^{-5}$ ). In EtOH the complex is light sensitive. The photolysis is accompanied by spectral changes (Fig. 2) which indicate the formation of  $[(\eta\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3]$ . At the isosbestic point ( $\lambda = 317 \text{ nm}$ )  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$  and  $[(\eta\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3]$  have the same



**Fig. 1** Electronic absorption (—) and emission (---) spectra of  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]\text{PF}_6$  at room temperature under argon. Absorption:  $5.63 \times 10^{-5} \text{ M}$  in EtOH, 1 cm cell. Emission: in MeCN,  $\lambda_{\text{exc}} = 380 \text{ nm}$ , intensity in arbitrary units.

absorption coefficient (4100). In a qualitative analysis protons and acetaldehyde are detected as further photoproducts. The progress of the photolysis was monitored by measuring the decrease of the optical absorption at 298 nm where the absorption coefficients of  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$  and  $[(\eta\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3]$  are 23 800 and 3700, respectively. The quantum yield of this photoreaction is  $\phi = 0.18$  at  $\lambda_{\text{irr}} = 366 \text{ nm}$ .

Complexes of the type  $[(\text{arene})\text{M}^0(\text{CO})_3]$  can be viewed as pseudo-octahedral  $d^6$  complexes in which the arene occupies three coordination sites at the central metal. The electronic spectra and photochemistry of a variety of such complexes have been studied in the past.<sup>3</sup> These compounds display  $\text{M}^0 \rightarrow \pi^*$  arene MLCT absorptions near 300 nm. However, LF excited states are apparently located below these MLCT states as indicated by the emission behavior and photochemical properties. While related complexes such as  $[\text{Re}^{\text{I}}(\text{bipy})(\text{CO})_3\text{Cl}]$  are characterized by lowest energy MLCT states which are luminescent under ambient conditions,<sup>3-5</sup>  $[(\text{arene})\text{M}^0(\text{CO})_3]$



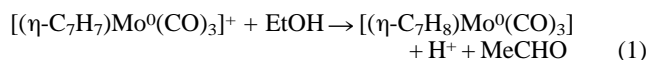
**Fig. 2** Spectral changes during the photolysis of  $1.06 \times 10^{-4} \text{ M}$   $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]\text{PF}_6$  in EtOH under argon at room temp. after 0 (a), 5 (b), 10 (c) and 20 s (d) irradiation time,  $\lambda_{\text{irr}} = 313 \text{ nm}$  (1 kW Xe/Hg 977 B-1 lamp), 0.1 cm cell

complexes are not emissive at room temperature and in solution.<sup>3,4</sup> The presence of lowest energy LF excited states is also consistent with the observation that these complexes undergo efficient photosubstitution reactions.<sup>3</sup>

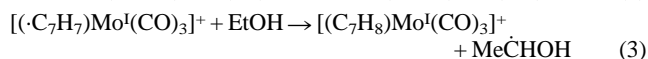
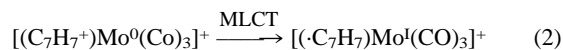
If arenes in  $[(\text{arene})\text{M}(\text{CO})_3]$  are replaced by the isoelectronic aromatic tropylium cation which is a strong electron acceptor<sup>6,7</sup> MLCT states should be shifted to lower energies and might now occur below the photoactive LF states. The results of the present study are in agreement with this expectation.

The rather intense absorption of  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$  at  $\lambda_{\text{max}} = 379$  nm (Fig. 1) is assigned to the  $\text{M}^0 \rightarrow \pi^*$   $\text{C}_7\text{H}_7^+$  MLCT transition. This band is scarcely solvent dependent. However, the strong interaction of the tropylium ligand with  $\text{Mo}^{10,13,15}$  is certainly associated with a considerable mixing of ligand and metal orbitals. Accordingly, the CT character should be reduced and the change of dipole moment during MLCT excitation might be quite small. On the other hand, the appearance of a room temperature emission is consistent with a MLCT assignment. It is assumed that the emitting state is a triplet in analogy to many other luminescing  $d^6$  complexes with metals of the second and third transition row.<sup>1-5</sup>

In ethanol  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$  undergoes a photoreduction according to eqn. (1).



This reaction consists of a hydride transfer from ethanol to the  $\text{C}_7\text{H}_7^+$  ligand yielding the cycloheptatriene complex and acetaldehyde. In the ground state only the reaction of  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$  with strong  $\text{H}^-$  donors such as  $\text{BH}_4^-$  generates the trialkene complex.<sup>12,13</sup> Although the mechanism of the photoreduction of coordinated  $\text{C}_7\text{H}_7^+$  to  $\text{C}_7\text{H}_8$  is unknown, it should be related to the nature of the reactive excited state. In the MLCT state the complex may be regarded as a  $\text{Mo}^{\text{I}}$  complex which contains a  $\text{C}_7\text{H}_7$  radical as a ligand. The  $\text{C}_7\text{H}_7$  radical should be able to abstract a hydrogen atom from ethanol [eqn. (3)].



The  $\text{Me}\dot{\text{C}}\text{HOH}$  radical is a strong reductant and transfers an electron to the oxidizing  $\text{Mo}^{\text{I}}$  complex yielding the final products.

In conclusion, it has been shown that  $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]^+$  is characterized by a lowest energy MLCT state which is luminescent and, in the presence of suitable substrates, also reactive.

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## Notes and References

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