

- 822 (29), 821 (18), 820 (47), 819 (59), 818 (76), 817 (82), 816 (94), 815 (100), 814 (88), 813 (94), 812 (65), 811 (47), 810 (41), 809 (35), 808 (24), 807 (18), 806 (18), 805 (12).  $\text{H}_2\text{FeRuOs}_2(\text{CO})_{13}$ : 911 (13), 910 (28), 909 (20), 908 (65), 907 (53), 906 (93), 905 (98), 904 (100), 903 (88), 902 (93), 901 (58), 900 (55), 899 (38), 898 (25), 897 (20), 896 (13), 895 (8).
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### Excited-State Reactivity Patterns of Hexakisarylisocyano Complexes of Chromium(0), Molybdenum(0), and Tungsten(0)

Sir:

The photochemical behavior of metal complexes possessing low-lying metal to ligand charge transfer (MLCT) excited states is poorly understood at present, owing to the virtual absence of systematic investigations on such systems.<sup>1</sup> For this reason we have initiated a research program aimed at the elucidation of the photochemistry of low-valent metal complexes containing arylosicyanide ligands. Many of these complexes exhibit intense visible absorption bands attributable to MLCT transitions,<sup>2</sup> and with third-row  $d^6$  metals such as W(0) and Re(I) there is reason to believe that these transitions are much less energetic than the lowest  $d-d$  excitation. Our studies to date have shown that the system comprised of hexakisarylisocyano complexes of Cr(0), Mo(0), and W(0) appears particularly promising from a photochemical standpoint. Accordingly, we communicate here the results of experiments that demonstrate the rich photochemical properties of this system.

Emission data from measurements of  $\text{ML}_6$  complexes ( $M = \text{Cr}(0), \text{Mo}(0), \text{W}(0)$ ;  $L = \text{CNPh}, \text{CNIph}$ ;  $\text{Ph} = \text{phenyl}, \text{Iph} = 2,6\text{-diisopropylphenyl}$ ) in pyridine at room temperature and in 2-MeTHF at 77 K are set out in Table I. Emission from the Mo(0) and W(0) complexes was also observed in 2-methylpentane, benzene, and 2-MeTHF solutions at room temperature. In each case the emission band is red-shifted and broadened in going from 77 to 298 K. Only extremely weak emission was observed for  $\text{Cr}(\text{CNIph})_6$  at 298 K in fluid solutions.

The low temperature emission band of each of the W(0) complexes overlaps an absorption system (at 550 nm in  $\text{W}(\text{CNPh})_6$ ) that is found on the low energy tail of the lowest intense feature (Figure 1). Similar behavior was observed for the Mo(0) complexes. The Cr(0) complexes exhibit much weaker and broader emissions than those seen in the Mo(0) and W(0) complexes; in each case this emission overlaps the lowest intense absorption band (Figure 2). The emission lifetimes in 2-methylpentane for the  $\text{M}(\text{CNIph})_6$  complexes are

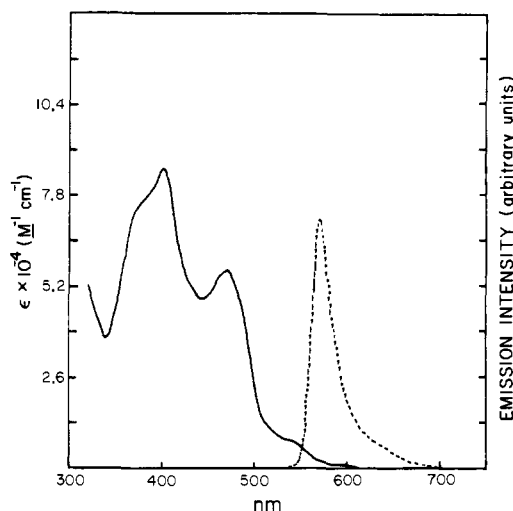
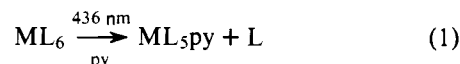


Figure 1. Absorption and emission spectra of  $\text{W}(\text{CNPh})_6$  in 2-MeTHF at 77 K.

as follows:  $\tau(\text{Cr}) < 10 \text{ ns}$ ,  $\tau(\text{Mo}) 40.2 \pm 0.5 \mu\text{s}$ ,  $\tau(\text{W}) 7.6 \mu\text{s}$  (77 K);  $\tau(\text{Mo}) 43 \pm 2 \text{ ns}$ ,  $\tau(\text{W}) 83 \pm 2 \text{ ns}$  (298 K). The much shorter lifetime for the Cr(0) complex suggests that in that case the emission is an allowed (singlet  $\rightarrow$  singlet)  $L\pi^* \rightarrow d\pi$  process. As the emissions from the Mo(0) and W(0) complexes have longer lifetimes, they probably represent  $L\pi^* \rightarrow d\pi$  transitions with triplet  $\rightarrow$  singlet character, although the designation of the lowest spin-orbit excited state as a "triplet" is undoubtedly a gross oversimplification.<sup>11</sup>

Irradiation of  $\text{ML}_6$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) in pyridine solutions at 436 nm gives photosubstitution (eq 1):<sup>3</sup>



The quantum yields decrease in an interesting pattern,  $[\text{Cr}(\text{CNPh})_6] (0.23) \sim [\text{Cr}(\text{CNIph})_6] (0.23) > [\text{Mo}(\text{CNPh})_6] (0.055) > [\text{Mo}(\text{CNIph})_6] (0.022) > [\text{W}(\text{CNPh})_6] (0.011) \gg [\text{W}(\text{CNIph})_6] (0.0003)$ . The lowering of the yield for substitution in going to the heavier metals and increased steric hindrance of the ligand suggests that for the Mo(0) and particularly for the W(0) complexes the mechanism has associative character.<sup>4</sup> That is, the small quantum yield for  $\text{W}(\text{CNPh})_6$ , which is drastically decreased in  $\text{W}(\text{CNIph})_6$ , may be accounted for by direct nucleophilic attack on the positively charged metal center in an MLCT state,  $[\text{M}^+(\text{CNPh})_6^-]^*$ . Such attack could not occur without great steric strain in  $\text{W}(\text{CNIph})_6$ . Our results for the two tungsten arylosicyanides, therefore, provide a convincing case for a bimolecular excited state substitution pathway, and stand in striking contrast to the many dissociative photosubstitution reactions that have been documented for  $\text{M}(\text{CO})_n$  ( $n = 4, 5, 6$ ) complexes.<sup>5,6</sup>

Irradiation of  $\text{M}(\text{CNIph})_6$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) in well-de-

Table I. Emission Data<sup>a</sup> for  $\text{ML}_6$  Complexes

Complex	77 K		298 K	
	$\lambda_{\text{max}}$ (nm) <sup>b</sup>	$\bar{\nu}_{\text{max}}$ (cm <sup>-1</sup> ) <sup>c</sup>	$\lambda_{\text{max}}$ (nm) <sup>b</sup>	$\bar{\nu}_{\text{max}}$ (cm <sup>-1</sup> ) <sup>c</sup>
$\text{Cr}(\text{CNPh})_6$	590 (400)	16 900 (1800)	Not obsd	Not obsd
$\text{Mo}(\text{CNPh})_6^d$	559 (450)	17 900 (1100)	613 (420)	16 300 (2700)
$\text{W}(\text{CNPh})_6^d$	571 (450)	17 500 (900)	638 (420)	15 700 (3200)
$\text{Cr}(\text{CNIph})_6$	583 (380)	17 200 (2100)	600 (380)	16 700
$\text{Mo}(\text{CNIph})_6$	568 (450)	17 600 (1200)	579 (450)	17 300 (2000)
$\text{W}(\text{CNIph})_6$	578 (400)	17 300 (1150)	578 (420)	17 300 (1800)

<sup>a</sup> All spectra were corrected for phototube and monochromator response; 77 K measurements were made in 2-MeTHF glasses; 298 K measurements were made in pyridine solutions. <sup>b</sup> Excitation wavelengths (nm) are given in parentheses. <sup>c</sup> Full widths (cm<sup>-1</sup>) at half-height are given in parentheses. <sup>d</sup> Quantum yields at 77 K are as follows: Mo,  $0.78 \pm 0.08$ ; W,  $0.93 \pm 0.07$  (excitation at 450 nm; measured relative to  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  yield of  $0.376 \pm 0.036$ , as reported by J. N. Demas and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 2841 (1971)).

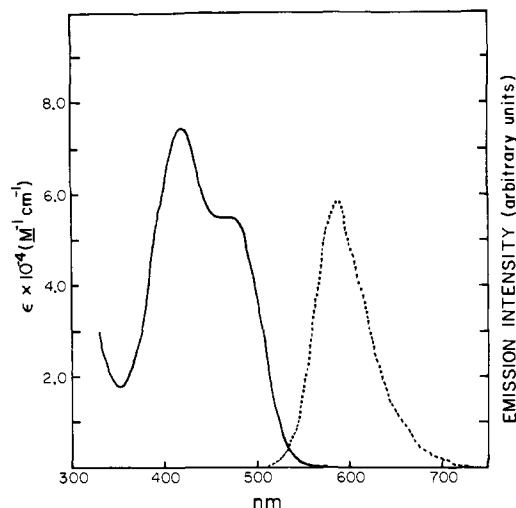
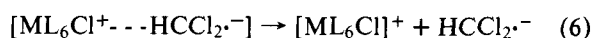
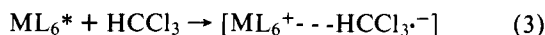


Figure 2. Absorption and emission spectra of  $\text{Cr}(\text{CNPh})_6$  in 2-MeTHF at 77 K.

gassed chloroform at  $\lambda$  436 nm gives the one-electron oxidation products  $\text{M}(\text{CNPh})_6^+$ .<sup>7</sup> Complexes of this type containing low-spin  $d^5$  Cr(I) have recently been prepared by thermal routes and characterized by Treichel and Essenschmayer.<sup>8</sup> The quantum yield for each of the three complexes is  $0.19 \pm 0.01$ . In the presence of oxygen this yield increases dramatically (with  $\text{M} = \text{Cr}$ , the yield at 436 nm is  $0.70 \pm 0.01$  in chloroform saturated with air).<sup>9</sup> Irradiation of  $\text{M}(\text{CNPh})_6$  ( $\text{M} = \text{Mo}, \text{W}$ ) produces seven-coordinate, two-electron oxidation products,  $[\text{M}(\text{CNPh})_6\text{Cl}]^+$ .<sup>10</sup> Molybdenum(II) complexes of similar composition have been characterized previously by Lippard and co-workers<sup>11</sup> as well as by Bonati and Minghetti.<sup>12</sup>

The above experimental results are consistent with the following mechanistic scheme:



The MLCT excited state formed (eq 2) is quenched by chloroform via electron transfer forming the radical pair  $[\text{ML}_6^{+-} \text{HCCl}_3 \cdot^-]$ .<sup>13</sup> This species can revert back to starting materials or undergo reaction. For  $\text{L} = \text{CNiPh}$ , the  $\text{HCCl}_3 \cdot^-$  radical presumably diffuses away, eventually releasing  $\text{Cl}^-$ . We propose that this step is rate controlling, thereby giving the constant quantum yield of 0.19 for the three metals.<sup>14</sup> In the complexes containing CNPh, which are much less hindered, we suggest that the chloroform radical anion transfers a chlorine atom to  $\text{ML}_6^+$  (eq 5), giving the seven-coordinate products that are observed for  $\text{M} = \text{Mo}, \text{W}$ .

**Acknowledgments.** We thank Edward Cuellar, Nathan Lewis, and Steve Milder for assistance with certain experiments. This research was supported by the National Science Foundation.

## References and Notes

- (1) Recent interest in this area, however, has been intense, and it is likely that our understanding of the reactivity of MLCT excited states will develop rapidly. See, for example: (a) J. Van Houten and R. J. Watts, *J. Am. Chem. Soc.*, **98**, 4853 (1976); (b) C. Creutz and N. Sutin, *Inorg. Chem.*, **15**, 496 (1976); (c) R. C. Young, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **98**, 286 (1976); (d) M. S. Wrighton, H. B. Abrahamson, and D. L. Morse, *ibid.*, **98**, 4106 (1976); (e) C. T. Lin, W. Böttcher, M. Chou, C. Creutz, and N. Sutin, *ibid.*, **98**, 6536 (1976); (f) C. Creutz and N. Sutin, *ibid.*, **98**, 6385 (1976); (g) C. Lin and N. Sutin, *J. Phys. Chem.*, **80**, 97 (1976); (h) R. E. Hintze and

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- (3) In each photoreaction release of one molecule of ligand was observed ( $\bar{\nu}(\text{CNPh})$  2125  $\text{cm}^{-1}$ ;  $\bar{\nu}(\text{CNiPh})$  2115  $\text{cm}^{-1}$  in infrared spectral experiments. Good isosbestic points were obtained in parallel visible absorption measurements.
- (4) However, the fact that the quantum yields for the two Cr(0) complexes are the same is consistent with a dissociative pathway for ligand substitution in those cases.
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- (6) For a discussion of the small amount of available evidence for bimolecular excited state processes involving certain substituted metal carbonyl complexes, see A. Vogler in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley-Interscience, New York, N.Y., 1975, Chapter 6.
- (7) The  $\text{Cr}(\text{CNiPh})_6^+$  complex was isolated and characterized as a  $\text{PF}_6^-$  salt. Anal. Calcd: C, 70.94; N, 6.22; H, 7.79. Found: C, 70.57; N, 6.36; H, 7.78.  $\nu(\text{C}\equiv\text{N})$ , Cr, 2065; Mo, 2050; W, 2040  $\text{cm}^{-1}$  ( $\text{CHCl}_3$  solution).
- (8) P. M. Treichel and G. J. Essenschmayer, *Inorg. Chem.*, **15**, 146 (1976).
- (9) Emission from  $\text{ML}_6$  complexes was found to be quenched in chloroform.
- (10) The  $[\text{Mo}(\text{CNPh})_6\text{Cl}]^+$  complex was isolated and characterized as a  $\text{Cl}^-$  salt. Anal. Calcd: C, 64.21; N, 10.70; H, 3.85. Found: C, 62.02; N, 10.66; H, 4.09.  $\nu(\text{C}\equiv\text{N})$ , Mo, 2100, 2130 (sh); W, 2100, 2130 (sh)  $\text{cm}^{-1}$  ( $\text{CHCl}_3$  solution). Irradiation of  $\text{Cr}(\text{CNPh})_6$  in degassed chloroform leads to a product which contains Cr(II) but does not correspond to either  $\text{Cr}(\text{CNPh})_6^{2+}$  or  $[\text{Cr}(\text{CNPh})_6\text{Cl}]^+$ .  $\text{Cr}(\text{CNPh})_6^{2+}$  has been prepared by Treichel and Essenschmayer.<sup>7</sup>
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- (13) It should be noted that no  $\text{ML}_6$  absorptions in  $\text{CHCl}_3$  solution attributable to metal to solvent transitions were observed in the visible region.
- (14) The large increase in yield in oxygenated chloroform solution for  $\text{Cr}(\text{CNiPh})_6^+$  formation could reflect the increased diffusion rate of  $\text{O}_2^-$ .

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## Crown Ether Model Systems for the Study of Photoexcited State Response to Geometrically Oriented Perturbers. The Effect of Alkali Metal Ions on Emission from Naphthalene Derivatives<sup>1</sup>

Sir:

Compounds **1** and **2** and a number of other new crown ether naphthalene derivatives<sup>1</sup> have been designed and synthesized to facilitate the study of the naphthalene chromophore and its response to a variety of perturbers. An important feature of these molecules is the predetermined orientation of the chromophore and a complexed perturber. In an exploratory study of alkali metal halide perturbation of **1** and **2**<sup>1-4</sup> we have found that these closely related naphthalene derivatives exhibit di-

Table I. Phosphorescence Lifetimes of 2,3-Naphtho-20-crown-6 (**1**) and 1,8-Naphtho-21-crown-6 (**2**) in 95% Ethanol Glass at 77 K with Alkali Halide Salts Added in 5:1 Molar Excess (crown at  $2.00 \times 10^{-4}$  F)

		$\tau_p$ (s)			$\tau_p$ (s)
<b>1</b> +	—	2.9	<b>2</b> +	—	2.45
	NaCl	3.4		NaCl	2.3
	KCl	3.1		KCl	1.4
	RbCl	2.7		RbCl	1.3
	CsCl	2.2		CsCl	1.2