

# Electronic Absorption Spectra and Phosphorescence of Oxygen-Containing Molybdenum(IV) Complexes

Ralph A. Isovitsch,<sup>†</sup> A. Scott Beadle, Frank R. Fronczek, and Andrew W. Maverick\*

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804

Received September 19, 1997

Electronic absorption and emission spectra are reported for salts of two oxomolybdenum(IV) cations,  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4]^+$  and  $[\text{MoOCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$ , and for the new Mo(IV) complex  $[\text{trans-Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4]^{2+}$ . All three ions show absorption bands ( $\lambda_{\text{max,abs}}$  550–570 nm;  $\epsilon$  45–120  $\text{M}^{-1} \text{cm}^{-1}$ ) attributable to the  $^1\text{A}_1[(d_{xy})^2] \rightarrow ^1\text{E}[(d_{xy})^1(d_{xz,yz})^1] (C_{4v})$  transition, and the last two show weak shoulders in the 700–750 nm range due to the analogous spin-forbidden ( $^1\text{A}_1 \rightarrow ^3\text{E}$ ) transition. Phosphorescence ( $\lambda_{\text{max,em}}$  850–960 nm) occurs in the solid state for all three compounds at both room temperature and 77 K, and for  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4]^+$  in  $\text{CH}_2\text{Cl}_2$  at room temperature. These are the first phosphorescences recorded for molybdenum(IV) complexes.  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$  precipitates quickly if  $\text{NaBPh}_4$  is added to the Mo(IV) solution prepared from  $\text{MoCl}_5$  and *tert*-butyl isocyanide in  $\text{CH}_3\text{OH}$ . However, if  $\text{NaPF}_6$  is used instead,  $[\text{trans-Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2$  (formed by reaction of  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4]^+$  with methanol) crystallizes over a period of ca. 24 h. The crystal structure of  $[\text{trans-Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2$  has been determined:  $\text{C}_{22}\text{H}_{42}\text{F}_{12}\text{MoN}_4\text{O}_2\text{P}_2$ , monoclinic; space group  $P2_1/c$ ;  $a = 9.1538(8) \text{ \AA}$ ,  $b = 15.709(2) \text{ \AA}$ ,  $c = 13.456(2) \text{ \AA}$ ;  $\beta = 103.31(1)^\circ$ ;  $Z = 2$ ;  $R(F) = 0.063$ ,  $R_w(F) = 0.056$  for 2719 reflections with  $I > \sigma(I)$ .

## Introduction

The photochemistry and photophysics of transition-metal complexes with multiply bonded main-group elements continues to be a rich area of study. Work in this area began with studies by Jørgensen and Gray and co-workers of the electronic structure of the molybdenyl ( $\text{MoV}^{3+}$ ) ion.<sup>1</sup> Since then, the photochemical and photophysical properties of numerous metal complexes with multiply bonded C, N, and O atoms have been explored. Of these, dioxo and nitrido complexes with the  $d^2$  configuration have been studied most often; examples include  $[\text{ReO}_2(\text{py})_4]^+$ ,  $[\text{OsNCl}_4]^-$ , and  $[\text{ReN}(\text{dmpc})_2\text{Cl}]^+$ .<sup>2–4</sup>

We have also been interested in *monooxo* complexes as chromophores. For example, the oxomolybdenum(V) complex  $[\text{MoOCl}_4(\text{NCCH}_3)]^-$  fluoresces in solution,  $^2\text{E}[(d_{xz,yz})^1] \rightarrow ^2\text{B}_2[(d_{xy})^1]$ , with a lifetime (110 ns) sufficient for reaction with one-electron oxidants and reductants.<sup>5</sup> We recently explored the reactivity of oxomolybdenum(V) with phosphines, and we showed that it oxidizes  $\text{PET}_2\text{Ph}$  and  $\text{PETPh}_2$  photochemically to their oxides.<sup>6</sup> Weak phosphorescence has also been demon-

strated for  $[\text{Re}^{\text{VO}}\text{Cl}_4(\text{CH}_3\text{CN})]^-$  and for solids containing  $[\text{Re}^{\text{VO}}\text{Cl}_5]^{2-}$ .<sup>7</sup> We wished to extend this work to oxomolybdenum(IV) complexes ( $d^2$ ), which might show phosphorescence as well. Herein we describe our work with the known oxomolybdenum(IV) complexes  $[\text{MoOCl}(\text{dppe})_2]^+$  ( $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) and  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4]^+$  and the new dimethoxomolybdenum(IV) complex  $[\text{trans-Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4]^{2+}$ . All three of these compounds phosphoresce in the solid state at room temperature and at 77 K, and  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4]^+$  also phosphoresces in solution at room temperature. We assign the emissions to the  $^3\text{E}[(d_{xy})^1(d_{xz,yz})^1] \rightarrow ^1\text{A}_1[(d_{xy})^2] (C_{4v})$  transition. As far as we are aware, this work represents the first demonstration of phosphorescence in molybdenum(IV) complexes. These complexes thus have potential as new chromophores for energy conversion and as new reagents for photochemical substrate transformations. The present complexes are more stable and they phosphoresce at higher energy and with longer lifetime than  $[\text{Re}^{\text{VO}}\text{Cl}_4(\text{CH}_3\text{CN})]^-$ .<sup>7a</sup> Also, the formation of  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4]^{2+}$  is an unusual example of the reaction of an oxo complex with an alcohol to give a dialkoxo species.

## Experimental Section

**Materials and Procedures.** All reactions and manipulations were performed using standard drybox techniques. Reagents and anhydrous solvents were of the highest commercial grade available. 1,2-Bis-(diphenylphosphino)ethane (dppe) was purchased from Organometallics, Inc. Benzylviologen dichloride (Sigma) was converted to its tetrafluoro-

<sup>†</sup> Present address: Division of Science and Mathematics, University of the Virgin Islands, St. Thomas, VI 00802.

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bororate salt,  $\text{BV}(\text{BF}_4)_2$ , by metathesis, as described by Mohammed et al.<sup>8</sup> Elemental analysis was performed by MHW Laboratories (Phoenix, AZ).

**Instrumentation.** FT-IR spectra were recorded in KCl disks on a Perkin-Elmer 1760X spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 300 MHz spectrometer; chemical shifts are reported in parts per million vs TMS.  $^{31}\text{P}$  NMR spectra were recorded on a Bruker 250 MHz spectrometer operating at 101.2 MHz; chemical shifts are reported in parts per million vs 85%  $\text{H}_3\text{PO}_4$ . Cyclic voltammetry was performed using a PAR model 174 polarographic analyzer, with degassed  $\text{CH}_2\text{Cl}_2/0.1\text{ M}$   $(\text{Bu}_4\text{N})(\text{O}_3\text{SCF}_3)$  as supporting electrolyte, Pt working and counter electrodes, and  $\text{Ag}/\text{AgCl}$  (saturated  $\text{NaCl}(\text{aq})$ ) reference electrode.

Electronic absorption spectra were recorded on an Aviv 14DS spectrophotometer. Emission spectra ( $\lambda_{\text{exc}}$  550 nm) were obtained by using a Spex Instruments Fluorolog 2 model F112X fluorometer, with a Hamamatsu R406 PMT; they were corrected for variation in detector response with wavelength. An Oxford Instruments model DN1704 cryostat, or a Pyrex dewar, was employed for low-temperature measurements. Lifetime measurements employed a Nd:YAG laser as excitation source (532 nm, second harmonic), with Schott colored-glass filters and a Spex 220M monochromator to isolate the emitted light. The emission signal from the photomultiplier tube (Hamamatsu R406) was passed to a Tektronix digitizing oscilloscope. Lifetimes were determined by exponential fits to the digitized phosphorescence decay curves.

**$[\text{MoOCl}(\text{dppe})_2](\text{BF}_4)$ .**<sup>9</sup>  $[\text{MoOCl}(\text{dppe})_2]\text{Cl}$  was prepared in methanol solution according to the literature procedure.<sup>10</sup> Treatment of this solution with excess methanolic  $\text{NaBF}_4$  produced a purple precipitate, which was recrystallized from methanol to give large, dark purple crystals.  $^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ ): 41.6.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ): 7.34, 7.15, 7.02 (m, 40H,  $\text{C}_6\text{H}_5$ ), 3.10, 2.83 (m, 8H,  $\text{CH}_2$ ). Anal. Calcd for  $\text{C}_{52}\text{H}_{48}\text{BClF}_4\text{MoOP}_4$ : C, 60.58; H, 4.69; Cl, 3.44. Found: C, 60.72; H, 4.88; Cl, 3.55.

***tert*-Butyl Isocyanide Complexes.** Both of these preparations began with a solution similar to that used by Novotny and Lippard<sup>11</sup> to synthesize  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{I}_3)$ .  $\text{MoCl}_5$  (1.0 g, 4 mmol) was dissolved in  $\text{CH}_3\text{OH}$  (15 mL) to give an emerald green solution. To this was added *tert*-butyl isocyanide (1.83 g, 22 mmol) all at once, causing the color to change to dark red.

**(a)  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$ .** The above Mo–CN-*t*-Bu mixture was stirred for 5–10 min, and then methanolic  $\text{NaBPh}_4$  (4 mmol) was added. The pale purple product precipitated promptly, and it was quickly collected, washed with diethyl ether, and dried in a vacuum desiccator. Yield: 1.0–1.1 g, 35–40%. IR: 2198 (CN), 952  $\text{cm}^{-1}$  (MoO).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 7.10 (m, 20H,  $\text{C}_6\text{H}_5$ ), 1.62 (s, 36H,  $\text{C}(\text{CH}_3)_3$ ). Anal. Calcd for  $\text{C}_{44}\text{H}_{56}\text{BClMoN}_4\text{O}$ : C, 66.13; H, 7.06; N, 7.01; Cl, 4.44. Found: C, 65.97; H, 7.22; N, 7.04; Cl, 4.63.

In addition to the absorption bands discussed below, samples of this complex sometimes showed a band at ca. 700 nm. The intensity of this band sometimes reached ca. 30% that of the 550 nm band, especially if the solid was allowed to stand in air for some time after preparation. We were unable to identify this impurity by IR or NMR. However, we selected samples with the smallest possible impurity concentrations, prepared without exposure to air, for the measurements reported here. These samples typically showed an absorbance at 700 nm <2% of that at 550 nm. The extinction coefficient at 550 nm and the phosphorescence intensity and lifetime were approximately the same for samples with larger and smaller amounts of the impurity.

**(b)  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2$ .** The red Mo–CN-*t*-Bu reaction mixture was stirred for 1 h. Then a solution of  $\text{NaPF}_6$  (1.84 g, 11 mmol) in 5 mL of  $\text{CH}_3\text{OH}$  was added. After continued stirring overnight, the brick-red reaction mixture had deposited a lavender, powdery precipitate, which was collected and then dissolved in  $\text{CH}_3$ -

**Table 1.** Crystal Data for  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2^{a,b}$

formula	$\text{MoC}_{22}\text{H}_{42}\text{N}_4\text{O}_2\text{P}_2\text{F}_{12}$
fw	780.47
space group	$P2_1/c$
Z	2
$\lambda/\text{\AA}$	0.710 73 (Mo K $\alpha$ )
$a/\text{\AA}$	9.1538(8)
$b/\text{\AA}$	15.709(2)
$c/\text{\AA}$	13.456(2)
$\beta/\text{deg}$	103.31(1)
$V/\text{\AA}^3$	1882.9(8)
$\rho_x/\text{g cm}^{-3}$	1.377
$\mu/\text{cm}^{-1}$	5.04
transm coeff	0.9499–0.9998
$R(F)$ (obsd data) <sup>b</sup>	0.063
$R_w(F)^c$	0.056

<sup>a</sup> In Tables 1–3, estimated standard deviations in the least significant digits of the values are given in parentheses. <sup>b</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ; data with  $I > \sigma(I)$ . <sup>c</sup>  $R_w = \sqrt{(\sum w(|F_o| - |F_c|)^2) / \sum w(F_o^2)}$ ;  $w = 4F_o^2 / (\sigma^2(I) + (0.02F_o^2)^2)$ .

**Table 2.** Selected Interatomic Distances/ $\text{\AA}$  and Angles/ $^\circ$  for  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2^a$

Mo–O1	1.791(3)	O1–C11	1.399(7)
Mo–C1	2.166(5)	C1–N1	1.134(7)
Mo–C6	2.173(4)	C6–N2	1.130(7)
O1–Mo–C1	93.6(2)	Mo–O1–C11	172.5(4)
O1–Mo–C1'	86.4(2)	Mo–C1–N1	170.9(4)
O1–Mo–C6	89.8(2)	Mo–C6–N2	175.1(4)
O1–Mo–C6'	90.2(2)	C1–N1–C2	176.3(5)
C1–Mo–C6	86.2(2)	C6–N2–C7	174.3(5)
C1–Mo–C6'	93.8(2)		

<sup>a</sup> Primes denote atoms related by the crystallographically imposed inversion center.

CN. The  $\text{CH}_3\text{CN}$  solution was filtered and then evaporated to yield lavender microcrystals of the product. Yield: 1.1 g, 40%. IR: 2213  $\text{cm}^{-1}$  (CN).  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ): 3.82 (s,  $\text{OCH}_3$ ), 1.68 (s,  $\text{C}(\text{CH}_3)_3$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ): 138.9 (CN), 70.9 ( $\text{OCH}_3$ ), 62.2, 30.7 ( $\text{C}(\text{CH}_3)_3$ ). Anal. Calcd for  $\text{C}_{22}\text{H}_{42}\text{F}_{12}\text{MoN}_4\text{O}_2\text{P}_2$ : C, 33.86; H, 5.42; N, 7.18. Found: C, 33.71; H, 5.52; N, 7.21. The  $^1\text{H}$  NMR integration for this compound was generally poor (ratio  $\text{C}(\text{CH}_3)_3:\text{OCH}_3$  found 6.4–8.9; calcd 6.0), but we found no evidence of impurities in NMR ( $^1\text{H}$  or  $^{13}\text{C}$ ); also, IR spectra ( $\nu_{\text{MoO}}$  region) showed no evidence for loss of the methoxo ligands.

**X-ray Analysis of  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2$ .** A crystal suitable for X-ray analysis was obtained by slow evaporation of a  $\text{CH}_3\text{CN}$  solution in a drybox. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer fitted with a Mo K $\alpha$  source and a graphite monochromator, using the  $\theta$ – $2\theta$  scan method; see summary in Table 1. Final unit cell constants were determined from the orientations of 25 centered high-angle reflections. The intensities were corrected for absorption using  $\psi$  scan data for five reflections. The MOLEN<sup>12</sup> set of programs was used. Structure solution was by direct methods; all non-hydrogen atoms were refined anisotropically, and H atoms were placed in calculated positions. Tables 2 and 3 list selected bond distances and angles and atomic coordinates. Complete X-ray information is available in CIF format via the Internet (see Supporting Information paragraph).

**Phosphorescence Quenching Experiments.** Solutions of  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$  (2 mM in acetone or 10 mM in  $\text{CH}_3\text{CN}$ ) were degassed by bubbling with  $\text{N}_2$ , and their phosphorescence intensities measured both with and without the addition of excess  $\text{BV}(\text{BF}_4)_2$  ( $\text{BV}^{2+}$  = benzylviologen (1,1'-dibenzyl-4,4'-bipyridinium)). Treatment with the benzylviologen salt usually produced a small amount of precipitate, which was removed by filtration, and a slight deepening of the purple color of the solution; however, spectral measurements showed that both chromophore and quencher remained present in the mixed solutions.

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**Table 3.** Positional Parameters and Their Estimated Standard Deviations for the Cation in  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2$ 

atom	x	y	z	$B_{\text{eq}}/\text{\AA}^2$
Mo	0.5	0.5	0.5	3.56(1)
O1	0.4429(4)	0.6062(2)	0.5214(2)	4.15(8)
N1	0.2200(4)	0.4027(3)	0.5681(3)	4.6(1)
N2	0.6631(5)	0.4822(2)	0.7448(3)	4.3(1)
C1	0.3088(5)	0.4423(3)	0.5432(4)	4.1(1)
C2	0.1128(6)	0.3472(4)	0.6018(4)	5.3(1)
C3	0.0848(8)	0.2738(4)	0.5278(5)	8.0(2)
C4	-0.0290(7)	0.3986(5)	0.5969(5)	8.1(2)
C5	0.1863(8)	0.3194(5)	0.7097(5)	10.0(2)
C6	0.6132(5)	0.4902(3)	0.6604(3)	4.4(1)
C7	0.7129(6)	0.4691(3)	0.8549(3)	4.4(1)
C8	0.8559(8)	0.4201(5)	0.8736(5)	8.3(2)
C9	0.5886(8)	0.4191(5)	0.8849(5)	8.4(2)
C10	0.7316(8)	0.5543(4)	0.9042(5)	8.0(2)
C11	0.4174(8)	0.6923(4)	0.5378(6)	9.3(2)

## Results and Discussion

**Synthesis and Characterization.** The preparation of the two oxomolybdenum(IV) complexes<sup>10,11</sup> depends on the addition of dppe or *tert*-butyl isocyanide to a Mo(V) solution to effect reduction to molybdenum(IV). All of the complexes studied here are purple, crystalline materials. They are air-stable in the solid state, with only  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2$  showing discoloration after several months. All of the complexes are stable in aerated solution for several days, except for  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$ , which appears to react slowly with air; see Experimental Section. In contrast, other oxomolybdenum(IV) complexes, such as  $[\text{MoOCl}_2(\text{PR}_3)_3]$ , are considerably more air- and water-sensitive.<sup>13–16</sup>  $[\text{MoOCl}(\text{dppe})_2](\text{BF}_4)$  is stable in a variety of solvents, whereas  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$  is most stable in  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , and acetone, and  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2$  is most stable in  $\text{CH}_3\text{CN}$ .

Novotny and Lippard isolated  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4]^+$  as its  $\text{I}_3^-$  salt.<sup>11</sup> The strongly colored  $\text{I}_3^-$  anion was likely to complicate a photophysical investigation of the molybdenum(IV) cation, so we attempted to isolate  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4]^+$  as the  $\text{BPh}_4^-$  and  $\text{PF}_6^-$  salts. Isolation of  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$  was successful when the reaction mixture was stirred for only a few minutes after the addition of the *tert*-butyl isocyanide, and methanolic  $\text{NaBPh}_4$  was used to induce immediate precipitation of the desired product.

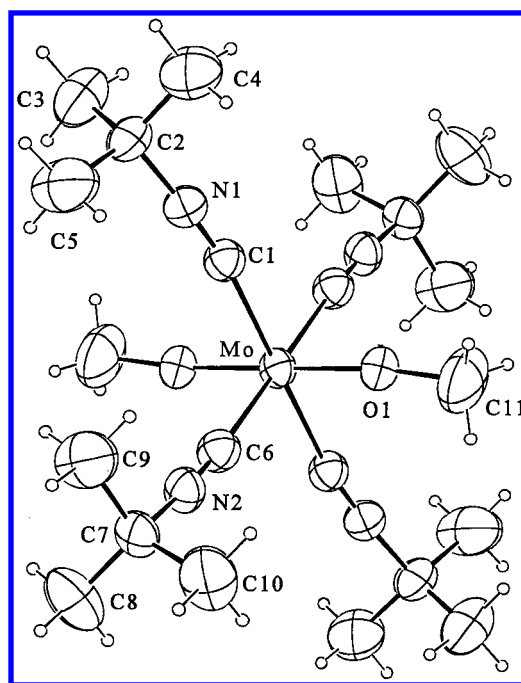
When we repeated this procedure with  $\text{PF}_6^-$  as the counterion, no precipitate formed at first; rather, a lavender solid formed over a period of 24 h. The electronic absorption and emission spectra of this material are similar to those of  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$  (see Tables 4 and 5), but its IR spectrum shows no absorption in the  $\nu_{\text{MoO}}$  region. X-ray analysis identified it as  $[\text{trans-Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2$  (see ORTEP<sup>17</sup> drawing in Figure 1).

The  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4]^{2+}$  cation is pseudooctahedral with four equatorial isocyanide ligands and two axial methoxy groups. The bonds to the equatorial isocyanide ligands are very similar in length to those in the oxomolybdenum(IV) complex

**Table 4.** Electronic Absorption Spectral Data for Mo(IV) and Related  $d^2$  Complexes

complex <sup>a</sup>	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/\text{M}^{-1}\text{cm}^{-1}$	solvent	ref
$[\text{MoOCl}(\text{dppe})_2]^+$	567	75	$\text{CH}_3\text{CN}$	this work
	310 sh <sup>b</sup>	4600		
$[\text{MoOCl}(\text{CN-}t\text{-Bu})_4]^+$	550	115	$\text{CH}_2\text{Cl}_2$	this work
	328	155		
$[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4]^{2+}$	558	45	$\text{CH}_3\text{CN}$	this work
	285 sh	1250		
$[\text{ReO}_2(\text{py})_4]^+$	415		pyridine	2
$[\text{ReN}(\text{dmpe})_2\text{Cl}]^+$	362	250	$\text{CH}_2\text{Cl}_2$	4
	257	2980		
	238	4000		
$[\text{ReOCl}_4(\text{NCCH}_3)]^-$	1170	40	$\text{CH}_3\text{CN}$	7a
	840	35		
$[\text{OsNCl}_4]^-$	493	93	$\text{CH}_2\text{Cl}_2$	3
	441	77		
$[\text{OsN}(\text{NH}_3)_4]^{3+}$	400	200	$\text{CH}_3\text{CN}$	27
$[\text{OsO}_2(\text{CN})_4]^{2-}$	370	300	$\text{CH}_3\text{CN}$	28
	317	1000		
$[\text{PhC}\equiv\text{WCl}(\text{CO})_2(\text{tmeda})]$	448	390	toluene	29a

<sup>a</sup> py = pyridine; dmpe =  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ ; tmeda =  $\text{Me}_2\text{NCH}_2\text{-CH}_2\text{NMe}_2$ . <sup>b</sup> sh = shoulder.

**Figure 1.** ORTEP<sup>17</sup> drawing of the Mo(IV) cation in  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2$ , with ellipsoids at the 40% level.

$[\text{MoOCl}(\text{CNCH}_3)_4](\text{I}_3)$  (average  $\text{Mo-C}$  2.16 Å).<sup>18</sup> The axial  $\text{Mo-OCH}_3$  bonds are longer than terminal  $\text{Mo}\equiv\text{O}$  bonds in six-coordinate complexes, which are typically 1.64–1.70 Å in length.<sup>18,19</sup> However, they are shorter than the  $\text{Mo-OH}_2$  bond in  $[\text{MoO}(\text{OH}_2)(\text{CN})_4]^{2-}$  (2.271(14) Å), the  $\text{Mo-OH}$  distance in  $[\text{MoO}(\text{OH})(\text{CN})_4]^{3-}$  (2.077(7) Å), and even the  $\text{Mo-O}$  distances in  $[\text{MoO}_2(\text{CN})_4]^{4-}$  (1.834(9) Å).<sup>20</sup> These comparisons suggest relatively strong  $\text{Mo-O}$   $\pi$  bonding in  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4]^{2+}$ , as does the nearly linear  $\text{Mo-O-C}$  bond angle. Strong  $\pi$  donation from the methoxy ligands is favored by the

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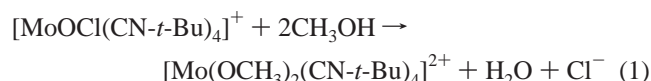
**Table 5.** Phosphorescence Data for Mo(IV) and Related d<sup>2</sup> Complexes

complex <sup>a</sup>	phosphorescence $\lambda_{\text{max}}/\text{nm}$		medium	ref
	300 K	77 K		
[MoOCl(dppe) <sub>2</sub> ] <sup>+</sup>	940	960	solid	this work
[MoOCl(CN- <i>t</i> -Bu) <sub>4</sub> ] <sup>+</sup>	860		CH <sub>2</sub> Cl <sub>2</sub>	this work
	ca. 800	788, 856, ca. 935	solid	
[Mo(OCH <sub>3</sub> ) <sub>2</sub> (CN- <i>t</i> -Bu) <sub>4</sub> ] <sup>2+</sup>	800, 854	780, 870, 930	solid	this work
[ReO <sub>2</sub> (py) <sub>4</sub> ] <sup>+</sup>	655		pyridine	2
[ReN(dmpe) <sub>2</sub> Cl] <sup>+</sup>	508		CH <sub>2</sub> Cl <sub>2</sub>	4
[ReOCl <sub>4</sub> (NCCH <sub>3</sub> )] <sup>-</sup>	ca. 1300		CH <sub>3</sub> CN	7a
[OsNCl <sub>4</sub> ] <sup>-</sup>		710 <sup>b</sup>	solid	3
[OsN(NH <sub>3</sub> ) <sub>4</sub> ] <sup>3+</sup>	545		CH <sub>3</sub> CN	27
		565, 600, 627, 688	solid	
[OsO <sub>2</sub> (CN) <sub>4</sub> ] <sup>2-</sup>	710		CH <sub>3</sub> CN	28
[PhC≡WCl(CO) <sub>2</sub> (tmeda)]	640		toluene	29a

<sup>a</sup> py = pyridine; dmpe = Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>; tmeda = Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>. <sup>b</sup> At 5 K.

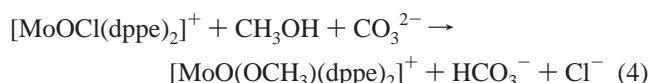
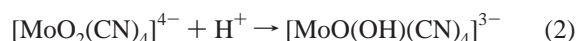
overall positive charge of the complex, as well as by the presence of the equatorial  $\pi$  acceptor ligands CN-*t*-Bu. Nearly linear M—O—C linkages are also found in [Mo<sup>IV</sup>O(OCH<sub>3</sub>)<sub>2</sub>(dppe)<sub>2</sub>][BPh<sub>4</sub>],<sup>21</sup> and in two oxo(alkoxo)rhenium(V) complexes,<sup>22</sup> although these all show M—OCH<sub>3</sub> distances longer than that in the present dimethoxomolybdenum(IV) cation. On the other hand, the tungsten(IV) complex [WCl<sub>2</sub>(OC<sub>6</sub>H<sub>3</sub>-2,6-Ph<sub>2</sub>)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>], which has no strong  $\pi$  acceptor ligands, shows longer W—O distances (1.966(4) Å) and more acute W—O—C angles (140.0(4)°).<sup>23</sup>

Thus, two different molybdenum(IV)—isocyanide complexes can be produced from the same reaction mixture. When BPh<sub>4</sub><sup>-</sup> is the counterion, the initially formed [MoOCl(CN-*t*-Bu)<sub>4</sub>]<sup>+</sup> ion is removed quickly by precipitation. On the other hand, [MoOCl(CN-*t*-Bu)<sub>4</sub>](PF<sub>6</sub>) is apparently substantially more soluble in the reaction mixture, and this allows time for reaction of [MoOCl(CN-*t*-Bu)<sub>4</sub>]<sup>+</sup> with methanol to give [Mo(OCH<sub>3</sub>)<sub>2</sub>(CN-*t*-Bu)<sub>4</sub>]<sup>2+</sup>, as in eq 1. The dimethoxo complex may be more



stable than the oxo complex under our conditions. Also, the lower solubility of [Mo(OCH<sub>3</sub>)<sub>2</sub>(CN-*t*-Bu)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub> in the reaction medium, as compared to [MoOCl(CN-*t*-Bu)<sub>4</sub>](PF<sub>6</sub>), may help to drive reaction 1 in the forward direction.

This reaction can be compared with other routes for the formation of alkoxo- or hydroxo-metal complexes with the d<sup>2</sup> configuration: proton transfer (an example is shown in eq 2),<sup>20</sup> alkylation (eq 3),<sup>22</sup> and ligand substitution (eq 4).<sup>10</sup> In all of these reactions, the product contains at least one metal-oxo bond; in contrast, our reaction in methanol converts one metal-oxo bond into two metal-alkoxo bonds. Reaction 1 is similar to the conversion of a ketone to its ketal, in that neither acid nor base is consumed.<sup>24</sup> The relatively strong Mo—O bonds in the dimethoxo complex (see above) may help to favor its formation in methanol solution.



As an alternative rationale for production of both [MoOCl(CN-*t*-Bu)<sub>4</sub>]<sup>+</sup> and [Mo(OCH<sub>3</sub>)<sub>2</sub>(CN-*t*-Bu)<sub>4</sub>]<sup>2+</sup> from the same solution, we considered the possibility that both cations are formed initially on reaction of Mo(V) with the isocyanide, and that BPh<sub>4</sub><sup>-</sup> precipitates the former and PF<sub>6</sub><sup>-</sup> the latter. However, we believe that this is unlikely, because this would not explain why the precipitation with PF<sub>6</sub><sup>-</sup> is slow, while that with BPh<sub>4</sub><sup>-</sup> is rapid. Also, the yield of the oxo complex is highest after a very short reaction time, whereas precipitation of the dimethoxo complex requires a number of hours; this suggests that eq 1 correctly describes the reaction occurring in these solutions.

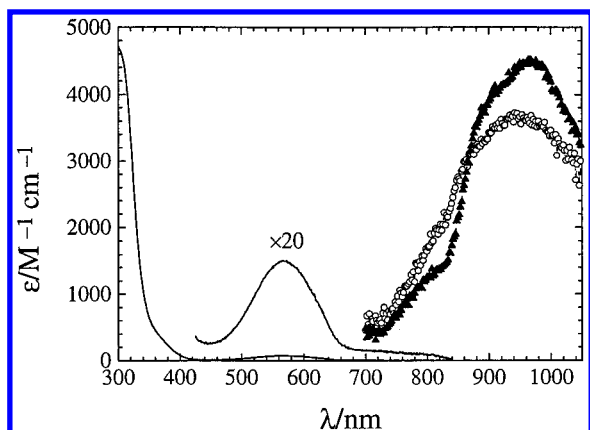
We also attempted to carry out the interconversions between the oxo and dimethoxo species using purified Mo(IV) complexes. For example, we dissolved crystalline [MoOCl(CN-*t*-Bu)<sub>4</sub>](BPh<sub>4</sub>) in methanol in order to study reaction 1 in the forward direction. In separate experiments, we added [Mo(OCH<sub>3</sub>)<sub>2</sub>(CN-*t*-Bu)<sub>4</sub>](PF<sub>6</sub>)<sub>2</sub> to methanol/HCl(aq) as a probe for the reverse reaction. Unfortunately, as mentioned above, neither of the complexes is stable in methanol for long periods of time: these solutions decomposed before any interconversion had occurred in either direction.

**Electronic Structure: Absorption Spectra.** We chose the present complexes for initial study in part because of their relatively high symmetry: all three have approximate C<sub>4v</sub> symmetry, as opposed to species such as *cis-mer*-MoOCl<sub>2</sub>(PR<sub>3</sub>)<sub>3</sub> (C<sub>2v</sub>). A qualitative energy diagram for the d orbitals in these complexes is shown in Scheme 1. With strong axial  $\pi$  donor ligands, the gap between d<sub>xy</sub> and d<sub>xz,yz</sub> is expected to be large, and a d<sup>2</sup> complex should have the ground state <sup>1</sup>A<sub>1</sub>[(d<sub>xy</sub>)<sup>2</sup>]. The lowest-energy transitions are to the <sup>3</sup>E and <sup>1</sup>E excited states, both arising from the (d<sub>xy</sub>)<sup>1</sup>(d<sub>xz,yz</sub>)<sup>1</sup> configuration; and the <sup>1</sup>A<sub>1</sub> → <sup>1</sup>E transition should be readily observable. This scheme has been used to discuss the spectra of a number of d<sup>2</sup> transition metal oxo and nitrido complexes.<sup>2,25,26</sup>

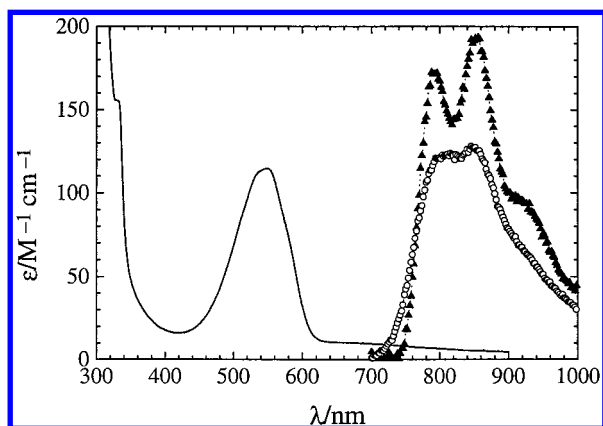
The present Mo(IV) complexes all exhibit an absorption in the visible at approximately 550 nm, as illustrated by the spectra

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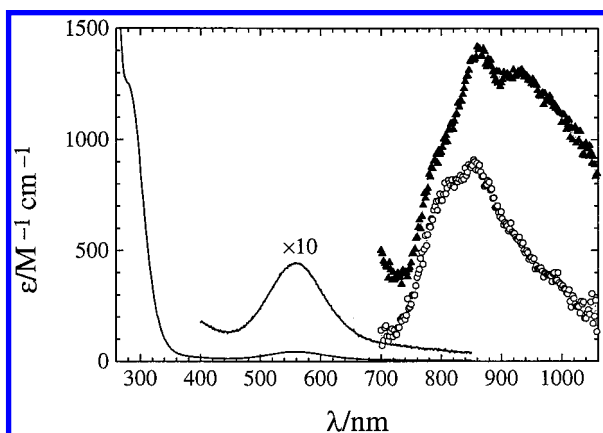
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**Figure 2.** Electronic spectra of  $[\text{MoOCl}(\text{dppe})_2][\text{BF}_4]$ . Absorption: —, 300 K,  $\text{CH}_3\text{CN}$  solution. Corrected phosphorescence (arbitrary units): ○, 300 K, solid; ▲, 77 K, solid.

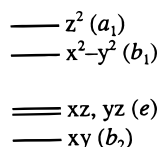


**Figure 3.** Electronic spectra of  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4][\text{BPh}_4]$ . Absorption: —, 300 K,  $\text{CH}_2\text{Cl}_2$  solution. Corrected phosphorescence (arbitrary units): ○, 300 K, solid; ▲, 77 K, solid.

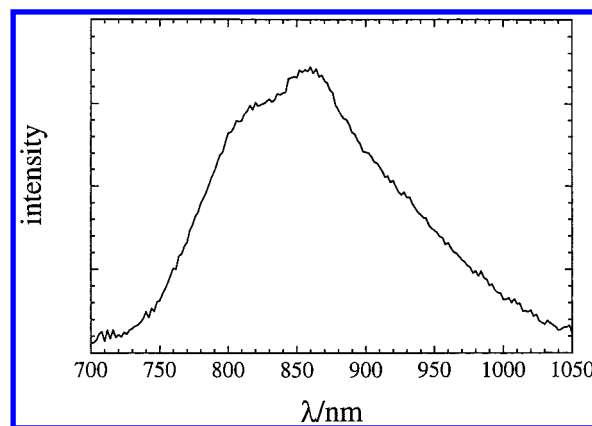


**Figure 4.** Electronic spectra of  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4][\text{PF}_6]_2$ . Absorption: —, 300 K,  $\text{CH}_3\text{CN}$  solution. Corrected phosphorescence (arbitrary units): ○, 300 K, solid; ▲, 77 K, solid.

**Scheme 1.** Energy Diagram ( $C_{4v}$ ) for  $\text{M}\equiv\text{O}$  and Related Complexes



in Figures 2–4. Maxima and extinction coefficients are listed in Table 4, with data for some similar Re and Os  $d^2$



**Figure 5.** Corrected phosphorescence spectrum of  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4][\text{BPh}_4]$  in  $\text{CH}_2\text{Cl}_2$  at room temperature.

complexes,<sup>2–4,7a,27,28</sup> and a closely related tungsten(IV) alkylidyne complex,<sup>29</sup> for comparison. Novotny and Lippard noted an absorption maximum at 547 nm ( $\epsilon = 124$ ) for  $[\text{MoOCl}(\text{CNCH}_3)_4](\text{PF}_6)$  in acetone,<sup>11</sup> very close to our values for  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$ . Dziegielewski observed this absorption band at 578 nm for  $[\text{MoOCl}(\text{dppe})_2]\text{Cl}$  in ethanol.<sup>30</sup> A band with similar position and intensity was also reported by Levason et al. for  $\text{W}^{\text{IV}}\text{OCl}(\text{dppe})_2^+$ .<sup>31</sup> We attribute these prominent low-energy bands to the  $^1A_1[(d_{xy})^2] \rightarrow ^1E[(d_{xy})^1(d_{xz,yz})^1]$  transition. The next-higher-energy transitions, beginning at 280–330 nm, are not well resolved in any of the complexes; their greater intensity indicates that they may have substantial charge-transfer character.

$[\text{MoOCl}(\text{dppe})_2](\text{BF}_4)$  and  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2$  also exhibit weak absorption bands ( $\epsilon < 10$ ) in the 700–800 nm region. These bands are attributable to the  $^1A_1[(d_{xy})^2] \rightarrow ^3E[(d_{xy})^1(d_{xz,yz})^1]$  transition. A similar absorption is also present in  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$ , but this may be due to small amounts of an impurity (see Experimental Section) and not entirely to the  $^1A_1 \rightarrow ^3E$  transition.

$[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4]^{2+}$  and the two oxo complexes have very similar absorption and emission spectra. This suggests that the two methoxy groups provide a  $\pi$ -donor environment nearly identical to that of one oxo group. In contrast, protonation or alkylation of a single oxo group, as in  $[\text{Re}^{\text{VO}}_2]^+$  complexes<sup>22</sup> or  $[\text{MoO}_2(\text{CN})_4]^{4-}$ ,<sup>32</sup> typically leads to a red shift of at least 100 nm in the  $d_{xy} \rightarrow d_{xz,yz}$  absorption band.

**Phosphorescence.** Solid samples of all three Mo(IV) complexes phosphoresce at room temperature and at 77 K; see data in Table 5. The emissions are more intense at 77 K in all cases.  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4]^+$  also phosphoresces in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and acetone solutions (see Figure 5) and in PMMA films at room temperature (PMMA = poly(methyl methacrylate)). However, we could not detect any emission from solutions ( $\text{CH}_3\text{-CN}$ ) or films (PMMA or PVA) containing either  $[\text{MoOCl}(\text{dppe})_2]^+$  or  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4]^{2+}$  (PVA = poly(vinyl

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acetate)). Our assignment of these emissions as phosphorescence,  $^3E[(d_{xy})^1(d_{xz,yz})^1] \rightarrow ^1A_1[(d_{xy})^2]$ , is supported by the large Stokes shifts between the prominent absorption and emission bands, and by emission lifetime data (see below).

Phosphorescence of  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$  in the solid state (Figure 3) and in  $\text{CH}_2\text{Cl}_2$  solution (Figure 5) is more intense than that of the other two complexes. At room temperature, the phosphorescence spectrum of solid  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$  exhibits poorly resolved vibrational fine structure, which becomes more distinct at 77 K, with maxima at 790, 855, and ca. 935 nm. The first two peaks at 77 K are separated by  $960\text{ cm}^{-1}$ , very close to the ground state  $\text{Mo}=\text{O}$  stretching frequency of  $952\text{ cm}^{-1}$ ; the third peak occurs with a similar spacing, but it is not well enough resolved for accurate measurement. Structured phosphorescence in nitridorhenium(V) complexes has been attributed to vibronic transitions;<sup>4</sup> detailed analyses of vibrational fine structure in absorption and emission have also been carried out on related dioxorhenium(V),<sup>2</sup> nitridoosmium(VI),<sup>3</sup> and oxomolybdenum(V)<sup>5b</sup> complexes.

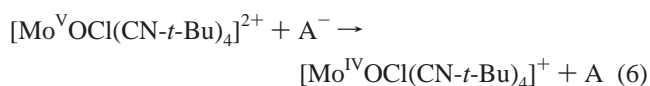
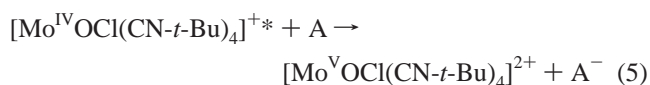
The phosphorescences of solid  $[\text{MoOCl}(\text{dppe})_2](\text{BF}_4)$  (Figure 2) and  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2$  (Figure 4) are broad, showing slight red shifts at 77 K. Especially at 77 K, the spectra show evidence for multiple maxima attributable to vibrational fine structure.

Pulsed-laser excitation (Nd:YAG, 532 nm) of the solid Mo(IV) complexes also induces phosphorescence. Emission decay curves were exponential for  $\text{CH}_2\text{Cl}_2$  solutions of  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$ , yielding a lifetime of  $2.5\text{ }\mu\text{s}$  ( $\pm 10\%$ ) at room temperature.

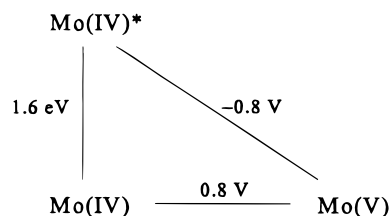
We were unable to measure lifetimes for the solid-state emissions: the phosphorescence decay curves were nonexponential, falling off more rapidly at first and then approaching exponential behavior at longer delay times. Approximate limiting lifetimes, estimated at the longest delay times, were as follows:  $[\text{MoOCl}(\text{dppe})_2](\text{BF}_4)$ ,  $1\text{ }\mu\text{s}$  at room temperature and  $1.5\text{ }\mu\text{s}$  at 77 K;  $[\text{Mo}(\text{OCH}_3)_2(\text{CN-}t\text{-Bu})_4](\text{PF}_6)_2$ ,  $2\text{ }\mu\text{s}$  at both room temperature and 77 K; and  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$ , ca.  $10\text{ }\mu\text{s}$  at room temperature and  $>30\text{ }\mu\text{s}$  at 77 K. Measurements with  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$  in PMMA films yielded approximately the same limiting lifetimes at room temperature and 77 K as those with the powder.

**Redox and Photoredox Properties.** Since  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4]^+$  phosphoresces in solution, we were also interested in whether it could undergo photoredox reactions. We first explored the electrochemical properties of the ion. Cyclic voltammetry experiments with  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$  in  $\text{CH}_2\text{Cl}_2$  revealed an irreversible oxidation wave at ca.  $0.8\text{ V}$  vs  $\text{Fc}/\text{Fc}^+$  (ca.  $1.25\text{ V}$  vs  $\text{Ag}/\text{AgCl}$ ), and no other waves within the stability range of the solvent. The simplest redox process that is consistent with this electrochemical behavior is one-electron oxidation of  $[\text{Mo}^{\text{IV}}\text{OCl}(\text{CN-}t\text{-Bu})_4]^+$  to  $[\text{Mo}^{\text{V}}\text{OCl}(\text{CN-}t\text{-Bu})_4]^{2+}$ , followed by rapid decomposition of the Mo(V) product.

If  $[\text{Mo}^{\text{IV}}\text{OCl}(\text{CN-}t\text{-Bu})_4]^+$  can be oxidized electrochemically, its phosphorescent excited state might also react with one-electron acceptors A. This would result in oxidative quenching of the excited state, as in reaction 5. In order for reaction 5 to



**Scheme 2.** Modified Latimer Diagram for  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4]^+$ <sup>a</sup>



<sup>a</sup> Redox potentials are in volts vs  $\text{Fc}/\text{Fc}^+$ ; excited state energy is in electronvolts.

be spontaneous, the redox potential for oxidation of the Mo(IV) excited state (i.e., for the  $\text{Mo(V)}/\text{Mo(IV)}^*$  couple) must be less than that for the  $\text{A}/\text{A}^-$  couple. The  $\text{Mo(V)}/\text{Mo(IV)}^*$  potential can be estimated from the ground-state redox potential and the energy of the excited state with the aid of the modified Latimer diagram shown in Scheme 2.

The energy of an excited state can be determined from the overlap of absorption and emission bands, with the aid of high-resolution spectral measurements at low temperature. However, in the present case, this information is not available. Instead, we can estimate the excited-state energy from the position of the high-energy "tail" of the luminescence band. The phosphorescence "tail" in Figure 3 is at ca.  $750\text{ nm}$  (ca.  $13\,300\text{ cm}^{-1}$ , or  $1.6\text{ eV}$ ). Thus, the excited-state redox potential ( $[\text{Mo}^{\text{IV}}\text{OCl}(\text{CN-}t\text{-Bu})_4]^+ / [\text{Mo}^{\text{V}}\text{OCl}(\text{CN-}t\text{-Bu})_4]^{2+}$ ) is ca.  $-0.8\text{ V}$  vs  $\text{Fc}/\text{Fc}^+$ , or ca.  $-0.35\text{ V}$  vs  $\text{Ag}/\text{AgCl}$ ; and the  $\text{A}/\text{A}^-$  couple should be more positive than  $-0.8\text{ V}$  vs  $\text{Fc}/\text{Fc}^+$ . (Since the wave we observed in cyclic voltammetry is irreversible, the redox potentials shown in the diagram are estimates; the actual values may be more negative, i.e., it may be easier to oxidize Mo(IV) than the diagram indicates.)

If A is neutral or anionic, then  $\text{A}^-$  will be an anion, and the electron-transfer products will have opposite charges, so that they are likely to remain closely associated after reaction 3 occurs. This will permit extremely rapid back electron transfer (reaction 4 above), making it difficult to observe  $\text{A}^-$  or Mo(V). The chances of observing these electron-transfer products are best if A is a cation. Among the most popular cationic oxidative quenchers in photoredox experiments are the viologens, because they are colorless and their one-electron-reduced forms are deep blue or violet.<sup>33</sup> The intense color of the reduced viologens makes confirmation of an electron-transfer reaction possible e.g. by spectral measurements in flash photolysis.

Benzylviologen,  $\text{BV}^{2+}$ , is one of the best oxidants in the viologen family ( $E_{1/2} = -0.76\text{ V}$  vs  $\text{Fc}^+/\text{Fc}$  in  $\text{CH}_3\text{CN}$ <sup>8</sup>), and it is also soluble in appropriate solvents. Addition of excess  $\text{BV}(\text{BF}_4)_2$  to solutions of  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4](\text{BPh}_4)$  in either acetone or acetonitrile gave solutions that still showed  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4]^+$  phosphorescence at approximately its original intensity. This indicates that  $\text{BV}^{2+}$  does not quench the phosphorescence of  $[\text{MoOCl}(\text{CN-}t\text{-Bu})_4]^+$  efficiently. An electron acceptor with a more positive redox potential would be more likely to quench the Mo(IV) phosphorescence, but we are not aware of any cationic acceptors with the right combination of redox potential and spectral properties appropriate for detection of electron transfer.<sup>34</sup>

**Comparison with other  $d^2$  and  $d^1$  systems.** The photochemical data for the present compounds may be compared with those for the other  $d^2$  systems in Tables 4 and 5, and with a representative fluorescent  $d^1$  complex,  $[\text{MoOCl}_4(\text{CH}_3\text{CN})]^-$ . All

of the  $d^2$  systems show excited-state lifetimes in the microsecond range, as compared with 110 ns for  $[\text{MoOCl}_4(\text{CH}_3\text{CN})]^-$ ,<sup>5a</sup> and less for other fluorescent  $d^1$  systems.<sup>5a,7a</sup> The  $d^2$  systems are expected to show longer lifetimes, since their emission is phosphorescence, while the  $d^1$  systems show only fluorescence. Likewise, the  $d^2$  systems show much larger Stokes shifts between their prominent absorption and emission bands than the  $d^1$ : 6400–7000  $\text{cm}^{-1}$  in our Mo(IV) complexes, and  $\geq 8000$   $\text{cm}^{-1}$  for Re(V) and Os(VI), vs 2800  $\text{cm}^{-1}$  in  $[\text{MoOCl}_4(\text{CH}_3\text{CN})]^-$ . This is also not surprising, because the prominent transitions in absorption and emission are different in  $d^2$  but the same in  $d^1$ . Finally, the energies of the  $d_{xy} \rightarrow d_{xz,yz}$  transitions are very similar in the Mo(V) and Mo(IV) monooxo systems, but substantially larger in the nitrido and dioxo complexes. This reflects the stronger  $\pi$  bonding of one N or two O atoms as compared to a single O atom.

(34) The neutral acceptors chloranil, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, and tetracyanoethylene are all significantly stronger oxidants than  $\text{BV}^{2+}$  (Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Solutions*; Dekker: New York, 1970). However, when we added these acceptors to solutions of  $[\text{MoOCl}(\text{CN}-t\text{-Bu})_4]^+$ , the color of the solutions changed substantially. This suggests that the more powerful acceptors form electron donor–acceptor charge-transfer complexes with the Mo(IV) complex, making the study of simple excited-state electron-transfer reactions impossible.

## Summary

The photophysical characteristics of the known oxomolybdenum(IV) complexes  $[\text{MoOCl}(\text{dppe})_2](\text{BF}_4)$  and  $[\text{MoOCl}(\text{CN}-t\text{-Bu})_4](\text{BPh}_4)$  and the new dimethoxomolybdenum(IV) complex  $[\text{Mo}(\text{OCH}_3)_2(\text{CN}-t\text{-Bu})_4](\text{PF}_6)_2$  have been explored. The crystal structure of  $[\text{Mo}(\text{OCH}_3)_2(\text{CN}-t\text{-Bu})_4](\text{PF}_6)_2$  has also been determined. All of these oxygen-containing  $d^2$  molybdenum complexes phosphoresce in the solid state at room temperature and at 77 K.  $[\text{MoOCl}(\text{CN}-t\text{-Bu})_4](\text{BPh}_4)$  also phosphoresces in solution at room temperature. We are now exploring the scope of phosphorescence in related Mo(IV)-oxo complexes, as well as their capacity for other photochemical reactions.

**Acknowledgment.** Support for improvements to the X-ray Crystallography Facility was provided by Grant LEQSF(1996-97)-ENH-TR-10, administered by the Louisiana Board of Regents.

**Supporting Information Available:** X-ray data for  $[\text{Mo}(\text{OCH}_3)_2(\text{CN}-t\text{-Bu})_4](\text{PF}_6)_2$ , in CIF format, is available on the Internet only. Access information is given on any current masthead page.

IC971186E