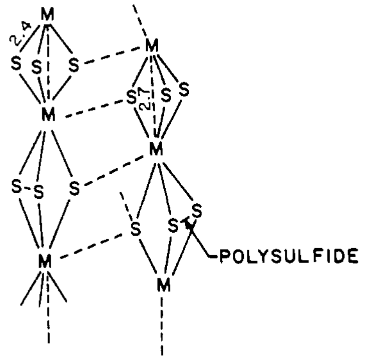

Figure 2. Proposed MoS_3 structure from Liang et al.[4]

talline group 4 and 5 trichalcogenides. Their results suggested that, in amorphous molybdenum trisulfide, the metal atoms are each coordinated by six sulfur atoms in a trigonal-prismatic environment, where each triangular face is shared by two metal atoms (see Figure 2). The results also indicated pairing of adjacent molybdenum atoms along the chain and presence of polysufide bonds. EXAFS studies[4] have shown the molybdenum is present in a pentavalent state, although magnetic susceptibility measurements[4] have indicated that MoS_3 is diamagnetic. These results are consistent with the formation of metal dimers. Infrared and Raman spectroscopy experiments[8] have provided further evidence for the presence of polysulfide bonds. The proposed molecular formula is $Mo^V(S^{2-})_2(S_2^{2-})_{1/2}$.

The EXAFS results on MoS_3 indicate that each molybdenum is coordinated to an average of 5.4 sulfur atoms at 2.41 Å. There are two different molybdenum–molybdenum coordination shells: the first at 2.74 Å with an average coordination of 1.4 and the second at 3.17 Å with an average coordination of 1.6. These results are in agreement with those reported elsewhere.[4]

The structural evolution of MoS_2 from MoS_3 would involve the breaking of the metal–metal bonds present in MoS_3 and formation of sheets like those in MoS_2. The molybdenum is also reduced from a pentavalent to a tetravalent state. The EXAFS results presented here indicate the presence of a small amount of an intermediate state with a molybdenum–molybdenum bond length of 3.02 Å (Table I). A simple model is to assume that the disulfide sulfur is lost, donating 1 mol of electrons/mol of molybdenum. The sulfur is lost on heating, resulting in a reduction of the molybdenum and lengthening of the metal–metal bond. As the sulfur is lost, the molybdenum atoms become coordinatively unsaturated, allowing the chains to rearrange into sheets. The molybdenum–sulfur coordination does not seem to change significantly, which is consistent with a low concentration of the intermediate state. The increase in coordination number of the Mo–Mo 3.16-Å distance reflects the formation of a two-dimensional MoS_2-like structure. The final Mo–Mo coordination number is reduced relative to crystalline MoS_2, suggesting the presence of small crystallites.

It is interesting to note the similarity between the poorly crystalline MoS_2 produced by thermal decomposition of MoS_3 and sulfided HDS catalysts. Figure 3 compares these two materials to crystalline MoS_2. All spectra were measured at 77 K, and data sets extend to 17.7 in *k*-space, yielding higher resolution Fourier transforms than those shown in Figure 1. The HDS catalyst is American Cyanimide HDS-2A sulfided in situ at 400 °C for 4 h with H_2S/H_2.[9] The sulfide catalyst structure is remarkably similar to that of amorphous MoS_2. Calculated coordination numbers are 4.0 for Mo–S coordination at 2.41 Å and 2.5 for Mo–Mo coordination at 3.16 Å. These reduced coordination numbers suggest the catalyst is composed of smaller crystallites than the amorphous MoS_2.

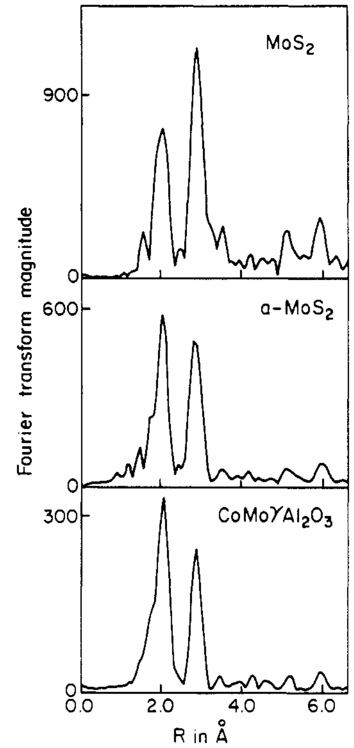

Figure 3. Magnitude of the Fourier transforms of EXAFS spectra after background subtraction and multiplication by k^3. All spectra were recorded at 77 K. The MoS_2 spectrum is the polycrystalline model compound; the amorphous MoS_2 spectrum is the product of the decomposition of MoS_3; the $Co/Mo/\gamma\text{-}Al_2O_3$ spectrum is the sulfide HDS catalyst.

Both poorly crystalline MoS_2 and sulfided $Co/Mo/\gamma\text{-}Al_2O_3$ show the 6.32-Å Mo–Mo shell. The amplitude of this peak in crystalline MoS_2 is twice that predicted by a single-scattering EXAFS model due to a multiple-scattering effect.[9] It is this amplitude increase that allows observation of this peak even in amorphous MoS_2. Its presence in sulfided $Co/Mo/\gamma\text{-}Al_2O_3$ strongly suggests that Mo is present as small relatively ordered MoS_2 crystallites.

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Registry No. MoS_3, 12033-29-3; MoS_2, 1317-33-5.

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High-Pressure Kinetic Evidence for Dissociative Activation during Substitution Reactions of Some Cobalt(III), Rhodium(III), and Chromium(III) Porphyrin Complexes in Aqueous Solution

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In a series of papers[2-7] it was demonstrated that axial-ligand substitution reactions of Co(III), Rh(III) and Cr(III) porphyrin complexes are significantly faster than normally observed for complexes of these metal ions.[8-10] For example, the anation reactions of *trans*-$M(TPPS)(OH_2)_2^{3-}$ (TPPS = *meso*-tetrakis(*p*-sulfonatophenyl)porphine) are approximately 10^9, 10^3, and 10^2 times faster than those of $M(NH_3)_5OH_2^{3+}$, where M = Co(III), Rh(III), and Cr(III), respectively.[6]

For the $Co(TPPS)(OH_2)_2^{3-}$ species, it was reported[5] that the formation constant for substitution by py, NCS^-, and I^- varied by a factor of 10^7, whereas the substitution rate constant varied only by a factor of 8. Furthermore, almost constant values for $\Delta H^‡$ and significantly positive values for $\Delta S^‡$ were found.[5] These data all imply a dissociative reaction mode. A similar tendency was reported[6] for the substitution reactions of $Co(TMPP)(OH_2)_2^{5+}$ (TMPP = *meso*-tetrakis(4-*N*-methylpyridyl)porphine). In addition, a good linear correlation between the formation constant and the aquation rate constant for a series of $Co(TMPP)(OH_2)L$ species led to the conclusion that the anation process follows an I_d mechanism.[6] Very recently, Tanaka and co-workers[11] reported the first high-pressure kinetic study of the substitution reactions of metalloporphyrins and presented evidence in favor of a dissociative reaction mechanism for the substitution of $Co(TMPP)(OH_2)_2^{5+}$ by NCS^-. They[11] reported a value of 14 ± 4 $cm^3\ mol^{-1}$ for the volume of activation for the formation of the $Co(TMPP)OH_2^{5+}$ five-coordinate intermediate, which strongly supports their mechanistic conclusion.

In contrast, mechanistic information on the substitution reactions of Rh(III) and Cr(III) prophyrins is rather vague and only tentative conclusions in terms of associative[3] and I_d[4,7] mechanisms, respectively, were reported. In an effort to gain insight into the intimate nature of such substitution processes and to elucidate the role played by the central metal ion, we have studied the effect of pressure on the substitution reactions of *trans*-$M(TPPS)(OH_2)_2^{3-}$ with NCS^- for M = Co(III), Rh(III), and Cr(III).

Experimental Section

The complexes $Na_3[Co(TPPS)(OH_2)_2]$, $Na_3[Rh(TPPS)(OH_2)_2]$, and $Na_3[Cr(TPPS)(OH_2)_2]$ were prepared and characterized as described before.[3-5] Chemicals of analytical reagent grade and doubly distilled water were used throughout the study. All rate measurements were done at an ionic strength of 1.0 M, controlled by the addition of $NaClO_4$, and in 0.1 M $HClO_4$. Kinetic runs were performed in a thermostated (±0.1 °C) high-pressure cell,[12] coupled to a Zeiss PMQ II spectrophotometer, or in a thermostated (±0.1 °C) high-pressure stopped-flow system.[13] The reactions were followed by monitoring the absorbance change at the Soret bands of the different complexes, i.e. 425, 417, and 444 nm for the Co(III), Rh(III), and Cr(III) complexes, respectively.[3-5] The observed first-order rate constants, k_{obsd}, were calculated from plots of ln $(A_t - A_\infty)$ vs. t, where A_t and A_∞ are the absorbances at time t and infinity, respectively. Such plots were linear for at least 2–3 half-lives of the reaction.

Results and Discussion

The substitution kinetics of the reactions under investigation were studied in detail at ambient pressure before.[2-4] It was shown that the overall reaction scheme is complicated due to the participation of diaquo, aquohydroxo, and dihydroxo complex species. In the present study the systems were significantly simplified by working in 0.1 M $HClO_4$ where only the diaquo species exist in solution.[2-5] The overall reactions can therefore be summarized as

Table I. k_1 as a Function of Pressure for the Anation of $Co(TPPS)(OH_2)_2^{3-}$ and $Rh(TPPS)(OH_2)_2^{3-}$ by NCS^- [a]

complex	T, °C	P, bar	k_1,[b] $M^{-1}\ s^{-1}$	$\Delta V^‡_{exptl}$, $cm^3\ mol^{-1}$
$Co(TPPS)(OH_2)_2^{3-}$	20	20	103 ± 2	15.4 ± 0.6
		250	90.0 ± 1.5	
		500	78.9 ± 2.2	
		750	65.1 ± 1.2	
		1000	55.0 ± 1.3	
$Rh(TPPS)(OH_2)_2^{3-}$	15	20	$(12.1 \pm 0.4) \times 10^{-3}$	8.8 ± 0.4
		250	$(11.0 \pm 0.1) \times 10^{-3}$	
		500	$(10.0 \pm 0.1) \times 10^{-3}$	
		750	$(9.03 \pm 0.30) \times 10^{-3}$	
		1000	$(8.45 \pm 0.12) \times 10^{-3}$	

[a] $[NCS^-] = 0.1$ M; $[Co(III)] = 4.2 \times 10^{-6}$ M; $[Rh(III)] = 4.7 \times 10^{-6}$ M; $[H^+] = 0.1$ M; ionic strength 1.0 M. [b] $k_{obsd} = k_1[NCS^-]$; mean value of at least six kinetic runs for the Co(III) complex and between three and four kinetic runs for the Rh(III) complex.

$$M(TPPS)(OH_2)_2^{3-} + NCS^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M(TPPS)(OH_2)NCS^{4-} + H_2O \quad (1)$$

$$M(TPPS)(OH_2)NCS^{4-} + NCS^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M(TPPS)(NCS)_2^{5-} + H_2O \quad (2)$$

Reaction 1 presents the rate-determining steps[2-4] such that

$$k_{obsd} = k_{-1} + k_1[NCS^-] \quad (3)$$

For the cases of M = Co(III) and Rh(III), the equilibrium constant K_1 $(=k_1/k_{-1})$ is such[2,3] that the reaction goes to completion and eq 3 can be simplified to

$$k_{obsd} = k_1[NCS^-] \quad (4)$$

This relationship was checked by measuring k_{obsd} as a function of $[NCS^-]$. Accordingly, the pressure dependence of k_1 was estimated from the pressure dependence of k_{obsd} at constant $[NCS^-]$, for which the results are summarized in Table I. In the case of M = Cr(III), K_1 is smaller[4] and the reaction does not go to completion. The pressure dependence of k_{obsd} was, therefore, studied as a function of $[NCS^-]$, and the results are reported in Table II. Plots of k_{obsd} vs. $[NCS^-]$ are linear at every pressure, and the pressure dependences of k_{-1} and k_1 were estimated from eq 3. Plots of ln k_1 and ln k_{-1} vs. pressure were linear in all cases, and the volumes of activation, $\Delta V^‡_{exptl}$ were estimated in the usual way[14] and are included in Tables I and II.

The values of k_1 and k_{-1} at 20 bar (Table III) are in close agreement with those reported at ambient pressure in the literature.[2-4] The large positive value of $\Delta V^‡_{exptl}(k_1)$ for the Co(III) complex parallels the positive value of $\Delta S^‡$ and can only be interpreted as evidence for a dissociative mechanism. This is in agreement with the high reactivity (stopped-flow rate) of this complex and the various arguments presented in the introduction. Furthermore, it is significant to note that $\Delta V^‡_{exptl}(k_1)$ is of the same order of magnitude as that reported by Tanaka et al.[11] for the $Co(TMPP)(OH_2)_2^{5+}$ species, and recent observations on the anation reactions of $Co(TAPP)(OH_2)_2^{5+}$ (TAPP = tetrakis(*p*-(trimethylammonio)phenyl)porphine) in this laboratory. These indicate that the overall

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Table II. k_{obsd} as a Function of Pressure for the Anation of $Cr(TPPS)(OH_2)_2{}^{3-}$ by NCS^- [a]

	10^4k_{obsd}, s^{-1}					
P, bar	$[NCS^-] = 0.2$ M	$[NCS^-] = 0.4$ M	$[NCS^-] = 0.6$ M	$[NCS^-] = 0.9$ M	10^4k_1, M^{-1} s^{-1}	10^4k_{-1}, s^{-1}
20	8.30 ± 0.03	10.1 ± 0.1	12.1 ± 0.1	14.9 ± 0.1	9.47 ± 0.11	6.38 ± 0.07
250	7.65 ± 0.05	9.18 ± 0.03	11.3 ± 0.1	13.8 ± 0.2	8.84 ± 0.31	5.81 ± 0.18
500	6.97 ± 0.33	8.60 ± 0.02	10.2 ± 0.1	12.7 ± 0.1	8.12 ± 0.02	5.34 ± 0.01
750	6.35 ± 0.07	7.88 ± 0.11	9.36 ± 0.03	11.7 ± 0.1	7.57 ± 0.02	4.84 ± 0.01
1000	6.00 ± 0.01	7.23 ± 0.06	8.85 ± 0.24	10.8 ± 0.1	6.95 ± 0.23	4.56 ± 0.14
$\Delta V^{\ddagger}_{exptl}$, cm^3 mol^{-1}					7.4 ± 0.1	8.2 ± 0.4

[a] $T = 15$ °C; $[Cr(III)] = 4.8 \times 10^{-6}$ M; $[H^+] = 0.1$ M; ionic strength 1.0 M. [b] Mean value of between two and four kinetic runs.

Table III. Summary of Rate and Activation Parameters for Substitution Reactions of the Type

$$M(TPPS)(OH_2)_2{}^{3-} + NCS^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M(TPPS)(OH_2)NCS^{4-} + H_2O$$

M	k_1, M^{-1} s^{-1}	k_{-1}, s^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal K^{-1} mol^{-1}	$\Delta V^{\ddagger}_{exptl}$, cm^3 mol^{-1}
Co(III)[a]	103 ± 2		18.4 ± 1.1[c]	+14.4 ± 3.7[c]	15.4 ± 0.6
Rh(III)[b]	$(12.1 \pm 0.4) \times 10^{-3}$		16.5 ± 0.2[d]	−10.3 ± 0.6[d]	8.8 ± 0.4
Cr(III)[b]	$(9.47 \pm 0.11) \times 10^{-4}$		16.8 ± 0.4[e]	−12.8 ± 1.4[e]	7.4 ± 0.1
		$(6.38 \pm 0.07) \times 10^{-4}$	15.7 ± 1.2[e]	−18.5 ± 4.2[e]	8.2 ± 0.4

[a] $T = 20$ °C. [b] $T = 15$ °C. [c] Data reported in ref 2. [d] Data reported in ref 3. [e] Data reported in ref 4.

charge on the complex plays a minor role in such processes. The suggested mechanism is outlined in

$$Co(TPPS)(OH_2)_2{}^{3-} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Co(TPPS)(OH_2)^{3-} + H_2O \xrightarrow[+NCS^-]{k_4} Co(TPPS)(OH_2)NCS^{4-} \quad (5)$$

For such a reaction scheme

$$k_{obsd} = k_3k_4[NCS^-]/(k_{-3} + k_4[NCS^-]) \quad (6)$$

which can be simplified to

$$k_{obsd} = k_3k_4[NCS^-]/k_{-3} \quad (7)$$

since it was observed that plots of k_{obsd} vs. $[NCS^-]$ were linear, indicating that $k_{-3} >> k_4[NCS^-]$. From eq 4 and 7, it follows that $k_1 = k_3k_4/k_{-3}$, such that $\Delta V^{*}_{exptl}(k_1) = \Delta V^{*}(k_3) + \Delta V^{*}(k_4) - \Delta V^{*}(k_{-3})$. This complicates the interpretation of $\Delta V^{*}_{exptl}(k_1)$ to some extent, since the contribution from the various reaction steps must be taken into consideration. $\Delta V^{*}(k_4)$ and $\Delta V^{*}(k_{-3})$ are both expected to be negative since they involve bond formation. It is also reasonable to assume that $|\Delta V^{*}(k_4)| > |\Delta V^{*}(k_3)|$ since ΔV^{*} is expected to depend on the partial molar volume of the entering ligand,[14] which is 40.2 and 18.0 cm^3 mol^{-1} for NCS^- and H_2O, respectively.[15] Furthermore, some charge concentration occurs during the k_4 reaction, which will further add to the overall negative value of $\Delta V^{*}(k_4)$ due to changes in solvation. In this respect it is important to note that the charge on the complex is spread over a planar surface area since the negatively charged sulfonato groups on the porphyrin ligand are removed from the metal center. It follows that the contribution of $(\Delta V^{*}(k_4) - \Delta V^{*}(k_{-3}))$ could be small but should be negative. On the other hand, the overall positive value of $\Delta V^{*}_{exptl}(k_1)$ indicates that $\Delta V^{*}(k_3)$ must outweight the latter contribution. This brings about the fact that $\Delta V^{*}(k_3)$ is at least as large as $\Delta V^{*}_{exptl}(k_1)$, and underlines the above arguments in favor of a dissociative reaction mechanism.

The values of $\Delta V^{*}_{exptl}(k_1)$ for the Rh(III) and Cr(III) complexes are significantly smaller than for the Co(III) complex and parallel the trend in the more negative ΔS^{*} values.[16,17] The change in sign of ΔS^{*} could be indicative of a change in mechanism down the series in Table III; however, the smaller differences in ΔV^{*}_{exptl} for M = Rh(III) and Cr(III) tend to rule out this possibility. A feasible reason for the smaller values of $\Delta V^{*}_{exptl}(k_1)$ could be a more negative contribution from $(\Delta V^{*}(k_4) - \Delta V^{*}(k_{-3}))$ than for the Co(III) complex. This would, for instance, require a more negative $\Delta V^{*}(k_4)$ value or less negative $\Delta V^{*}(k_{-3})$ value. Alternatively, the tendency can be interpreted as evidence for a dissociative interchange (I_d) mechanism in case of the Rh(III) and Cr(III) complexes. This possibility is outlined in

$$M(TPPS)(OH_2)_2{}^{3-} + NCS^- \overset{K_5}{\rightleftharpoons} (M(TPPS)(OH_2)_2{}^{3-},NCS^-) \xrightarrow{k_6} M(TPPS)(OH_2)NCS^{4-} + H_2O \quad (8)$$

$$M = Rh(III), Cr(III)$$

For such a mechanism

$$k_{obsd} = k_6K_5[NCS^-]/(1 + K_5[NCS^-]) \quad (9)$$

which simplifies to

$$k_{obsd} = k_6K_5[NCS^-] \quad (10)$$

because no curvature in the k_{obsd} vs. $[NCS^-]$ plots was observed and K_5 is expected to be very small. It follows that $k_1 = k_6K_5$ and $\Delta V^{*}_{exptl}(k_1) = \Delta V^{*}(k_6) + \Delta \bar{V}(K_5)$. Since the preequilibrium involves the concentration of charges, $\Delta \bar{V}(K_5)$ can be assumed[17,18] to be close to zero or slightly negative, such that $\Delta V^{*}_{exptl}(k_1) \lesssim \Delta V^{*}(k_6)$. It follows that the experimentally observed values are in good agreement with those expected for an interchange mechanism in which the rate-determining step is dissociatively activated.[14,17]

Similar arguments can be applied to interpret $\Delta V^{*}_{exptl}(k_1)$ for the aquation of $Cr(TPPS)(OH_2)NCS^{4-}$, which is almost identical with that for the anation process. This similarity also shows up in the other activation parameters, and we conclude

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that the aquation process also follows an I_d mechanism.

Finally, the results of this investigation clearly demonstrate how the presence of the porphyrin ligand promotes a dissociative reaction mode along the axial ligands and so accounts for the reactivity difference mentioned before.[2–7] The electron-rich porphine presumably donates electron density to the Co(III) ion making it more like Co(II) and so stabilizes the five-coordinate intermediate.[6] This is also seen in the completely different pressure dependencies found in this study compared to earlier results on the substitution reactions of the corresponding pentaammineaquo species.[19] The central metal atom seems to control the extent to which the porphyrin can modify the reactivity and mode of the substitution process.

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Registry No. *trans*-Co(TPPS)$(OH_2)_2^{3-}$, 58881-09-7; *trans*-Rh(TPPS)$(OH_2)_2^{3-}$, 66035-54-9; *trans*-Cr(TPPS)$(OH_2)_2^{3-}$, 33339-70-7; NCS^-, 302-04-5.

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Synthesis and Characterization of Six- and Seven-Coordinate Chloromolybdate(IV) Chelates

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Appropriate conditions have been found for the synthesis of the previously unknown MoL_3Cl chelates, where L = the anion of picolinic acid or an 8-quinolinol derivative. MoL_2Cl_2 chelates, where L is a uninegative bidentate ligand with either nitrogen and oxygen donors or all oxygen donors, have been known for many years;[1–3] however, no matter whether these virtually insoluble MoL_2Cl_2 complexes were synthesized from $MoCl_4$,[1,2] $MoCl_4 \cdot 2CH_3CN$,[3] $MoCl_5$,[2] or $MoCl_3(py)_3$,[3] further replacement of chloride by the chelating ligand was *not* observed in the earlier investigations. Complexes with three bidentate sulfur donors and a chloro donor are known, but they are formed by indirect routes.[4,5] Attempts to prepare the 8-quinolinol derivatives by one of these routes were also unsuccessful.[4] We have found that the more soluble MoL_3Cl species are formed by straight metathetical procedures if time, temperature, and ligand concentrations are sufficient. We wish to report the synthesis and characterization of these new species along with some new six-coordinate chelates with either an MoL_2Cl_2 or an $MoL'Cl_2$ formulation, where L′ = a quadridentate ligand with two negative charges.

Experimental Section

Reagents. Hexane (Baker, practical grade), methanol (ACS Certified Spectranalyzed), methylene chloride (Fisher, ACS Certified grade), and toluene (Fisher, ACS Certified grade) were dried and deoxygenated by heating under reflux conditions for 4 h over calcium hydride followed by distillation from calcium hydride under nitrogen. Chloroform (Fisher, laboratory grade) was deoxygenated by bubbling nitrogen through it for 1 h immediately prior to use. Absolute ethanol (USI Industrial Chemicals, USP grade) was used without further purification. Salicylaldehyde (MCB, practical grade) and *o*-phenylenediamine dihydrochloride (Eastman, practical grade) were used without further purification. 5,7-Dichloro-8-quinolinol (Aldrich), 5,7-dibromo-8-quinolinol (Aldrich), and 5-nitro-8-quinolinol (Aldrich) were purified by sublimation in vacuo at 150 °C. 5-Chloro-8-quinolinol (Aldrich) was purified by recrystallization twice from ethanol followed by sublimation in vacuo at 110 °C. 8-Quinolinol (Mallinckrodt) was purified by sublimation in vacuo at 80 °C. Picolinic acid (Eastman, practical grade) was purified by sublimation in vacuo at 80 °C. Molybdenum tetrachloride (some samples from Climax Molybdenum) was synthesized by a scale-up of the method of Moore and Larson[2] with some modifications.[6] Anal. Calcd for $MoCl_4$: Cl, 59.64; C, 0.00; H, 0.00. Found: Cl, 59.87; C, 0.32; H, <0.10.

Preparations of Complexes. General Procedures. All reactions were performed under an atmosphere of prepurified nitrogen. Transfers and operations involving $MoCl_4$, solutions of these complexes, or solid complexes containing significant traces of solvent were performed either in a glovebag or a drybox under an atmosphere of prepurified nitrogen. All solutions were stirred with a magnetic stirring bar in the flask.

Dichlorobis(5,7-dichloro-8-quinolinolato)molybdenum(IV), Mo(dcq)$_2$Cl$_2$. In a typical reaction, 1.03 g of molybdenum tetrachloride (4.33 mmol) and 1.86 g of 5,7-dichloro-8-quinolinol (8.69 mmol) in 150 mL of methylene chloride were heated with stirring under reflux conditions for 3 h. The resulting brown solution was filtered, and the brown precipitate was transferred to a Soxhlet extractor and extracted with methylene chloride until the extracting solvent was clear (ca. 18 h). The red-brown insoluble residue was dried in vacuo at 150 °C for 20 h; yield 1.16 g, 46.0%. The product is a red-brown homogeneous powder under a microscope at 400×. Anal. Calcd for $MoC_{18}H_8N_2O_2Cl_6$: C, 36.5; H, 1.4; N, 4.7; Cl, 35.9. Found: C, 36.0; H, 1.4; N, 4.5; Cl, 35.8. The compound is too insoluble to purify further.

Dichlorobis(8-quinolinolato)molybdenum(IV). First, 1.40 g of molybdenum tetrachloride (5.89 mmol) and 2.60 g of 8-quinolinol (17.91 mmol) in 300 mL of toluene were heated with stirring under reflux conditions for 4 h. The solution was then allowed to cool and was filtered, giving a yellow filtrate and a brown solid, which was extracted with methylene chloride in a Soxhlet-type extractor until the extracting solvent was clear (ca. 144 h). The brown insoluble residue was washed with two 10-mL portions of hot toluene and one 10-mL portion of methylene chloride. The light red-brown residue was dried in vacuo at 150 °C for 15 h. The product appears as a brown homogeneous powder under a microscope at 400×. Anal. Calcd for $MoC_{16}H_{12}N_2O_2Cl_2$: C, 47.5; H, 2.7; N, 6.2; Cl, 15.6. Found: C, 47.0; H, 2.7; N, 5.9; Cl, 14.9. The compound is very insoluble.

Dichlorobis(5-chloro-8-quinolinolato)molybdenum(IV). Initially, 0.84 g of molybdenum tetrachloride (3.53 mmol) and 1.27 g of 5-chloro-8-quinolinol (7.07 mmol) in 300 mL of toluene were heated with stirring under reflux conditions for $5^1/_2$ h. The resulting yellow-brown solution was filtered, giving a yellow solution and a red-brown solid, which was extracted in a Soxhlet extractor with methylene chloride until the extraction solution was light yellow (ca. 15 h). The insoluble orange residue was dried in vacuo for 18 h at 150 °C; yield 1.62 g, 70%. It appears as an orange-brown homogeneous powder under a microscope at 400×. Anal. Calcd for $MoC_{18}H_{10}N_2O_2Cl_4$: C, 41.25; H, 1.93; N, 5.35; Cl, 27.06. Found: C, 41.26; H, 2.16; N, 5.11; Cl, 26.81.

Dichloro(*N*,*N*′-disalicylidene-1,2-diaminobenzene)molybdenum(IV). First, 1.04 g of molybdenum tetrachloride (4.38 mmol) and 1.80 g of *N*,*N*′-disalicylidene-1,2-diaminobenzene (8.76 mmol) in 150 mL of toluene were heated with stirring under reflux conditions for 2 h. The solution was pale yellow with a dark brown precipitate. The solvent was then removed under vacuum, and the brown residue was

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