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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extracted with methylene chloride in a Soxhlet-type extractor until the extracting solvent was clear (ca. 24 h). The brown insoluble residue was dried in vacuo at 150 °C for 24 h; yield 0.64 g, 24%. It appears as a brown homogeneous powder under a microscope at 400×. Anal. Calcd for $MoC_{20}H_{14}N_2O_2Cl_2$: C, 49.91; H, 2.94; N, 5.82; Cl, 14.73. Found: C, 49.75; H, 3.23; N, 5.88; Cl, 14.71.

Chlorotris(5,7-dichloro-8-quinolinolato)molybdenum(IV), Mo(dcq)$_3$Cl. First, 1.70 g of molybdenum tetrachloride (7.15 mmol) and 4.57 g of 5,7-dichloro-8-quinolinol (21.4 mmol) in 200 mL of toluene were heated with stirring under reflux conditions for 5 h. The solvent was removed under vacuum, and the dark brown residue was transferred to a glovebox. This material was dissolved in 500 mL of toluene, the volume was reduced to 100 mL, and the solution was allowed to sit at room temperature for 24 h. The solution was then filtered, and the black crystalline precipitate was washed with three 10-mL portions of toluene. The product was dried in vacuo at 160 °C for 36 h; yield 4.1 g, 74%. Under a microscope at 400×, this material appears as a black crystalline solid. However, very thin crystal fragments appear red to transmitted light. Anal. Calcd for $MoC_{27}H_{12}N_3O_3Cl_7$: C, 42.08; H, 1.57; N, 5.45; Cl, 32.30. Found: C, 42.07; H, 1.52; N, 5.40; Cl, 32.02.

Chlorotris(5-nitro-8-quinolinolato)molybdenum(IV), Mo(nq)$_3$Cl. For this reaction, 0.88 g of molybdenum tetrachloride (3.70 mmol) and 2.81 g of 5-nitro-8-quinolinol (14.8 mmol) in 300 mL of methylene chloride were heated under reflux conditions with stirring for 16 h. The resulting solution was dark brown. The solvent was removed under vacuum. The brown residue was then washed with hot toluene until the washes were translucent (about 150 mL of toluene). These brown washes were combined, and the volume of solution was reduced to about 15 mL. The solution was then allowed to sit at room temperature for 24 h and was filtered, giving the reddish crystalline material, which was washed with two 3-mL portions of toluene. The product was dried in vacuo at 150 °C for 20 h; yield 0.11 g, 6%. The product appears as dark yellow-brown crystals under a microscope at 400×. Anal. Calcd for $MoC_{27}H_{16}N_6O_9Cl$: C, 46.40; H, 2.17; N, 12.03; Cl, 5.07. Found: C, 46.65; H, 2.41; N, 11.79; Cl, 5.07.

Chlorotris(5,7-dibromo-8-quinolinolato)molybdenum(IV), Mo(dbq)$_3$Cl. This was synthesized in the same manner as Mo(dcq)$_3$Cl; yield 20%. Under a microscope at 400×, the product appears as dark red needles. Anal. Calcd for $MoC_{27}H_{12}N_3O_3ClBr_6$: Mo, 9.2; C, 31.26; H, 1.17; N, 4.05; halide, 6.77 mequiv. Found: Mo, 9.4; C, 30.32; H, 1.10; N, 3.80; halide, 6.75 mequiv.

Chlorotris(picolinato)molybdenum(IV), Mo(pic)$_3$Cl. First, 1.00 g of molybdenum tetrachloride (4.21 mmol) and 3.07 g of picolinic acid (24.9 mmol) in 300 mL of toluene were heated with stirring under reflux conditions. After 65 h the red-brown slurry was allowed to cool and was filtered, giving a yellow solid and a light red filtrate. The yellow solid was washed with three 10-mL portions of toluene and dried in vacuo at 150 °C for 20 h; yield 2.26 g, 88%. The red solution was reduced in volume to about 10 mL and allowed to sit at room temperature for 24 h. A bronze-colored crystalline material precipitated from the solution and was collected and washed with a small amount of toluene. Comparison by infrared spectroscopy[7] and thin-layer chromatography of this complex showed it to be Mo(pic)$_4$;[8] yield 0.05 g, 2%. The primary Mo(pic)$_3$Cl product appears as a yellow homogeneous solid under a microscope at 400×. Anal. Calcd for Mo(pic)$_3$Cl, $MoC_{18}H_{12}N_3O_6Cl$: C, 43.43; H, 2.43; N, 8.44; Cl, 7.12. Found: C, 43.49; H, 2.56; N, 8.45; Cl, 7.12.

Characterization. The infrared spectra of all of the complexes synthesized were recorded on a Beckman IR-10 spectrophotometer. The reflectance and absorption electronic spectra were recorded on a Cary 14 spectrophotometer.

Magnetic susceptibility measurements were obtained by the Faraday method using a Cahn automatic electrobalance. [HgCo(CNS)$_4$] was used as a calibration standard. Corrections were made for paramagnetism in the sample dish and the diamagnetism of the ligands.[9] Conductivity measurements were made on an Industrial Instruments conductivity bridge. The conductivities of solutions of both KI and Mo(dcq)$_3$Cl in mixtures consisting of CH_2Cl_2 and CH_3OH were measured. The solvents were purified as described earlier and were deoxygenated by bubbling nitrogen through them for 30 min prior to use. The solutions were prepared and studied in a glovebag under an atmosphere of nitrogen.

Table I. Reaction between $MoCl_4$ and Hdcq under Various Reaction Conditions

stoichiometry[a]	solvent	reacn time, h	% yield		ratio of products
			bis	tris	
2.7:1	toluene	4	10	60	1:6
3:1	toluene	1	1	80	1:80
3:1	CH_2Cl_2	1	28	19	3:2
3:1	CH_2Cl_2	5	3	71	1:24
2:1	CH_2Cl_2	3	46	18	5:2

[a] Ligand to $MoCl_4$ mole ratio.

Table II. Conditions for Reactions of $MoCl_4$ with Bidentate Ligands

ligand	stoichiometry	solvent	time, h	% yield	
				bis	tris
Hq	3:1	toluene	4	51	23
Hcq	2:1	CH_2Cl_2	3	20	5
Hcq	2:1	toluene	6	78	
Hnq	3:1	toluene	5	20	3
Hnq	3:1	CH_2Cl_2	16	40	6
Hpic	3:1	CH_2Cl_2	3	*a*	*a*
Hpic	3:1	toluene	5	30	70
Hpic	3:1	toluene	22	10	90
Hpic	4:1	toluene	65	0	~98[b]

[a] Side reactions only. [b] The reaction appeared to be nearly quantitative even though some losses occurred during workup of the product and about 2% Mo(pic)$_4$ was isolated from this reaction.

Table III. Infrared Spectra[a] of MoL_xCl_y Complexes in the 270–400-cm^{-1} Region

Mo(q)$_2$Cl$_2$	286 w sh, 300 m, 339 m, 392 m
Mo(q)$_2$Cl$_2$[b]	300 sh, 312 sh, 325 sh, 330 sh, 345 sh, 400 m
Mo(cq)$_2$Cl$_2$	308 m, 345 w, 400 w
Mo(dcq)$_2$Cl$_2$	273 w, 311 m, 340 m, 400 m
Mo(dsp)Cl$_2$	275 w, 299 m, 345 m, 380 w
Mo(acac)$_2$Cl$_2$[c]	312 m, 342 s, 420 m
Mo(acac)$_2$Cl$_2$[b]	288 sh, 300 sh, 308 sh, 345 sh
Mo(dcq)$_3$Cl	296 w, 312 m, 390 m
Mo(pic)$_3$Cl	326 s, 400 m
Mo(dcq)$_4$	280 m, 400 m
MoCl$_4$(pz)$_2$[d]	306 sh, 330 sh
MoCl$_4$(quinoxaline)$_2$[d]	320, 341

[a] Frequencies reported in cm^{-1}; w = weak, m = medium, s = strong, sh = shoulder. [b] Reference 1. [c] Reference 3. [d] Reference 13.

Results and Discussion

Trischelated monochloro complexes MoL$_3$Cl are formed quite easily by using our conditions. Separation of the bischelated product is achieved on the basis of insolubility in all common organic solvents; it is isolated by filtration and is purified by Soxhlet extraction.

In order to better understand the general reaction, the $MoCl_4$–Hdcq reaction was studied in detail as summarized in Table I. As expected, the tris product is favored by longer reaction times, higher temperatures, and high ligand to $MoCl_4$ mole ratios.

Frazer and Goffer[10] have studied the reaction of 8-quinolinol with covalent metal halides. From reactions with titanium tetrachloride, they were able to isolate Ti(q)$_2$Cl$_2$ and Ti(q)$_3$Cl as well as titanium complexes with neutral 8-quinolinol, $TiCl_4$·Hq, and $TiCl_4$·2Hq. The protonated quinolinol was

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Table IV. Electronic Spectra of Chloromolybdenum Complexes[a]

$Mo(dcq)_3Cl$	$Mo(dbq)_3Cl$	$Mo(nq)_3Cl$	$Mo(pic)_3Cl$	$Mo(dcq)_2Cl_2$	$Mo(dsp)Cl_2$
[16] sh	[16] sh	[16] sh			
		19 sh[c]			
[20]	[20]	[19] sh	[20] sh		
20.5 (16)	20.6 (13)	20.5 (10)	20.4[b]		
		[21.2]		[21.3]	
		21.2 (7)[c]			
[25] sh	[25] sh	[25]	[25] sh		[24] sh
		25.0 (11)[c]	25.3[b]		
28.3 (9)	28.2 (8)	28.2 (5)			
30.0 (12)				[30]	
31.0 (12)			37.6[b]		

[a] Spectra in 10^3 cm^{-1} for chloroform solutions with molar extinction coefficients (10^3 cm^{-1} M^{-1}) in parentheses; Nujol mull reflectance/diffuse transmission spectra in square brackets; sh = shoulder. [b] CH_2Cl_2 solution. [c] Toluene solution.

postulated to act as a monodentate ligand through the nitrogen. These 8-quinolinol adducts were readily converted to $Ti(q)_2Cl_2$ upon heating. The mechanism proposed by these authors can be adapted to the $MoCl_4$ reaction with Hdcq with minor adjustments. Since $MoCl_4$ is insoluble in the solvents used in this reaction, the initial reaction is a surface reaction. The reactivity of $MoCl_4$ was found to be dependent upon the method of its synthesis. $MoCl_4$ synthesized according to the procedure of McCann and Brown[11,12] is less reactive than the $MoCl_4$ synthesized by the method of Moore and Larson.[2]

Reactions with Hdcq never proceed beyond the tris-substituted product, although a trace (2%) of the tetrakis-substituted product is obtained with the more acidic picolinic acid as the ligand (see Table II). If the substitution steps in this reaction are dependent on initial coordination of the aromatic nitrogen, coordination saturation (for spin-free d^2) and steric hindrance in $Mo(dcq)_3Cl$ might keep further substitution from occurring. However, conductivity measurements indicate facile dissociation of the chloro ligand; thus, initial coordination by the heterocyclic nitrogen of the fourth quinolinol ligand should be no problem. When the ligand is neutral, it apparently cannot compete with chloride for the seventh site, but the more nucleophilic deprotonated ligand allows the formation of a spin-paired eight-coordinate chelate. Thus, $Mo(dcq)_4$ is formed in the presence of a base.[6]

Functional groups on the quinolinol rings tend to increase solubility; for example, $Mo(dcq)_3Cl$ > $Mo(cq)_3Cl$ >> $Mo(q)_3Cl$. The poor solubility of the picolinate ligand in toluene slows its reactivity, but decomposition in the more polar CH_2Cl_2 precludes its use.

We have synthesized an $ML'Cl_2$ species, where L' is a quadridentate Schiff-base ligand. $Mo(dsp)Cl_2$ has properties similar to those of the other dichloromolybdenum species synthesized. It is a brown solid, is insoluble in most solvents, is hydrolyzed by water, and is slightly air sensitive.

In order to demonstrate the potential for these reactions with tungsten(IV) halides, this reaction was accomplished with $WCl_4(py)_2$ and H_2dsp. The infrared spectrum of the product of this reaction is essentially identical with that of $Mo(dsp)Cl_2$.

Infrared Spectra. Table III lists the bands observed in the region 270–420 cm^{-1} for a variety of MoL_xCl_y complexes. All of the new MoL_2Cl_2 species possess two peaks, one about 300–310 cm^{-1} and one about 335–345 cm^{-1}. These two bands were previously assigned to Mo–Cl stretches by both Doyle[3] and West[1] and are consistent with the Mo–Cl stretch for K_2MoCl_6 at 340 cm^{-1} [14] and the peaks observed at about 310 and about 340 cm^{-1} in MoL_2Cl_4 complexes.[13] Furthermore, the new MoL_3Cl species and $Mo(dcq)_4$ have one and zero Mo–Cl stretches, respectively. No Mo–Cl stretch is observed for $Mo(nq)_3Cl$ in this region, which suggests this complex may have a different solid-state structure than other MoL_3Cl complexes, perhaps containing bridging chloro ligands. In the well-resolved spectrum of $Mo(dcq)_2Cl_2$, and in those of several other MoL_2Cl_2 complexes, a peak is observed at 273 cm^{-1}, but it is also observed in a number of eight-coordinate complexes without chlorine[6] and therefore cannot be assigned as a Mo–Cl stretch.

Table V. Conductivity of $Mo(dcq)_3Cl$ vs. KI

solvent compn		conductivity, cm^2 Ω^{-1} equiv^{-1}	
% CH_2Cl_2	% CH_3OH	$Mo(dcq)_3Cl$	KI
50	50	109	112
60	40	79	94
70	30	64	91

In the 1000–1700-cm^{-1} region, patterns similar to the spectra of the ligands with slight shifts due to coordination are observed. Oxomolybdenum species have a strong absorbance in the region 900–1000 cm^{-1};[15] however, the coordinated dcq$^-$ ligand shows a sharp ligand peak at 969 cm^{-1} in the spectrum of a sample of $Mo(dcq)_2Cl_2$ that is analytically pure. Peaks are also observed at 924 and 970 cm^{-1} in pure $Mo(dsp)Cl_2$; thus, the association of peaks in the region 900–1000 cm^{-1} with Mo=O bands should be made with caution.

Electronic Spectra. The solution spectra of $Mo(dcq)_3Cl$, $Mo(dbq)_3Cl$, and $Mo(nq)_3Cl$ in $CHCl_3$ are dominated by a strong ($\epsilon \sim 10^4$) band in the visible region at about 20 500 cm^{-1} (485 nm) (Table IV). The large extinction coefficient of this band and its position at relatively low energy permit the assignment of this absorption as a charge-transfer band, though it is somewhat surprising that the band is not shifted in energy upon changing ligands from $Mo(dcq)_3Cl$ to $Mo(nq)_3Cl$. This band may be either a metal-to-ligand or a ligand-to-metal charge-transfer transition. Three transitions at higher energy exist in the electronic spectrum of $Mo(dcq)_3Cl$. The bands at 30 000 and 31 000 cm^{-1} are assigned as ligand transitions analogous to $W(dcq)_4$[16] and $Mo(dcq)_4$.[6] The reflectance and toluene solution spectra of $Mo(nq)_3Cl$ possess a strongly absorbing band centered at 21 200 cm^{-1} in addition to the maxima observed for $Mo(dcq)_3Cl$ and $Mo(dbq)_3Cl$. The spectrum of $Mo(dcq)_3Cl$ in toluene is the same as in chloroform so the difference is not a solvent effect. It is evident that the structure of $Mo(nq)_3Cl$ in the solid state and in toluene

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Table VI. Magnetic Moments[a] of Chloromolybdenum Complexes

$Mo(dcq)_3Cl$	2.71 (2.39)	$Mo(dcq)_2Cl_2$	2.62 (2.42)
$Mo(pic)_3Cl$	2.70	$Mo(cq)_2Cl_2$	2.78
$Mo(nq)_3Cl$	1.87	$Mo(q)_2Cl_2$	2.53

[a] Magnetic moments in Bohr magnetons at 294 K with selected values in parentheses for 77 K.

is somewhat different from those of the other MoL_3Cl complexes studied; cf. infrared spectral section above.

Conductivity Measurements. These measurements were very difficult to obtain due to the tendency of $Mo(dcq)_3Cl$ to oxidize in polar solvents. However, the data in Table V indicate that the $Mo(dcq)_3Cl$ complex is completely dissociated and acts as a one-to-one electrolyte just like KI; however, as the polarity decreases, the degree of ion pairing increases at a greater rate than that of KI, even though the large complex ion should not attract chloride that well by electrostatic considerations. This suggests that the molybdenum species is a six-coordinate $Mo(dcq)_3^+$ complex in polar solvents and is a seven-coordinate species with coordinated chloride in nonpolar solvents. Two seven-coordinate monochloro complexes of tungsten(II) show analogous behavior.[19] Unfortunately, solubility and stability considerations do not allow measurements a wider range of polarities.

Magnetic Moments. The magnetic moments for all of the complexes are slightly below the spin-only value for a d^2 system because of spin-orbit coupling (Table VI) and are consistent with the moments obtained for MoL_2Cl_2 complexes[1] and also that obtained for $Mo[S_2P(OR)_2]_3Cl$.[5] The magnetic moment of 2.53 μ_B for $Mo(q)_2Cl_2$ is within experimental error of the 2.58 μ_B value reported by the Australian workers for this complex.[1]

Although Moss and Shaw[17] were able to correlate magnetic moment with coordination number for six-coordinate *trans*-$WCl_4(PMe_2Ph)_2$ and seven-coordinate $WCl_4(PMe_2Ph)_3$, for the complexes in this study it was not possible to clearly distinguish between the six- and seven-coordinate complexes on the basis of magnetic properties. The moments for all of the complexes, with the exception of $Mo(nq)_3Cl$, lie between 2.5 and 2.8 μ_B, and the magnetic moments of $Mo(dcq)_3Cl$ and $Mo(dcq)_2Cl_2$ show similar temperature dependence. The complexes are of such low symmetry that arguments based on ground-state symmetry[17,18] for the complexes are not valid.

The magnetic moment of $Mo(nq)_3Cl$ is anomalous. The moment is below that of other spin-free Mo(IV) complexes. This observation, combined with the lack of any observable terminal Mo–Cl stretching vibration in the solid-state infrared spectrum and the solvent dependence of the electronic spectra, provides evidence that the monomeric seven-coordinate complex exists in chloroform and dimerizes to a chlorine-bridged eight-coordinate species in the solid state and in toluene. Proof of such a structure, however, awaits a more detailed study.

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Registry No. $Mo(q)_2Cl_2$, 36470-65-2; $Mo(cq)_2Cl_2$, 87739-28-4; $Mo(dcq)_2Cl_2$, 74594-57-3; $Mo(dsp)Cl_2$, 87739-29-5; $Mo(dcq)_3Cl$, 74620-90-9; $Mo(pic)_3Cl$, 87739-32-0; $Mo(dcq)_4$, 87739-33-1; $Mo(dbq)_3Cl$, 87739-31-9; $Mo(nq)_3Cl$, 87739-30-8.

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Electronic Effects on the Orientation of H_2 Addition to an Iridium(I) Complex

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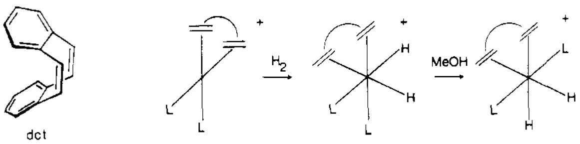
Hydrogen addition to d^8 metal complexes is an important step in hydrogenation and hydroformylation catalysis. We studied the factors that determine which of several possible isomers is formed on H_2 addition to Ir(I) complexes. This might influence the course of catalysis in asymmetric hydrogenation,[2] for example.

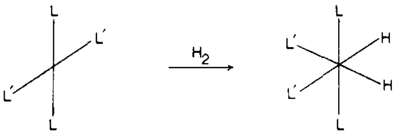
In a concerted addition, the two hydrides would normally be expected to occupy mutually cis positions in the product. A possible counterexample[3] has now been satisfactorily rationalized on the basis of cis addition.[4]

When several isomers having cis hydrides are possible, it is not always the thermodynamically most stable isomer that is formed. For example, we have shown that $[(dct)IrL_2]BF_4$

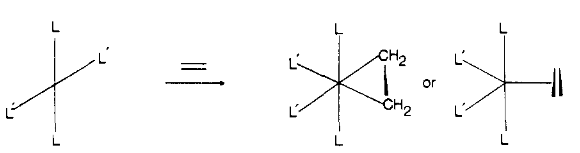


dct 1 2 3 (1)

(**1**: dct = dibenzo[*a*,*e*]cyclooctatetraene; L = PPh_3) adds H_2 to give a cis dihydride (**2**) in CH_2Cl_2 at –30 °C, but on addition of a trace of a weak base (e.g., MeOH), this isomer rearranges by a deprotonation/reprotonation mechanism to give the thermodynamically more stable cis,trans isomer (**3**).[5] This has mutually cis hydrides but cannot be formed from **1** directly if only processes of the type shown in eq 2 are invoked. An



(2)



4a 4b (3)

analogy can be seen to exist between the H_2 addition process of eq 2 and the addition of a simple 2-electron donor such as an olefin (eq 3) to give **4**. In each case, two trans ligands L′ fold back as the incoming 2-electron donor H_2 or C_2H_4 approaches. The olefin adduct could be considered a 6-coordinate M(III) (**4a**) complex or a 5-coordinate M(I) complex (**4b**). Structure **4a**,[6] the metallacyclopropane model, makes the analogy with the dihydride clearer.

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