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The resolution of CpMo(NO)(methylallyl)(X) complexes. X-ray crystal structures of (−)-CpMo(NO)(*syn*-crotyl)((1*S*)-10-camphorsulfonate) and $(\mu\text{-OH})_2[\text{CpMo(NO)I}]_2$ ☆

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Abstract

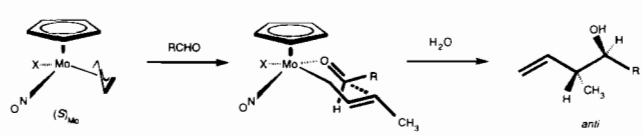
The resolution of the chiral metal center in CpMo(NO)(*syn*-crotyl)((1*S*)-10-camphorsulfonate) has been effected by fractional crystallization. An X-ray crystal structure determination of the (−)-diastereomer reveals an (*S*) configuration at the metal. It crystallizes from chloroform as a solvate having a formula of $MoCl_3SO_5NC_{20}H_{28}$ and in an orthorhombic cell with a space group of $P2_12_12_1$ with dimensions $a=7.039(1)$, $b=9.2797(6)$, $c=38.254(5)$ Å, $V=2498.8(6)$ Å^3 and $Z=4$. A partial kinetic resolution of racemic CpMo(NO)(η^3-2-MeC_3H_4)I has been carried out by reaction with (*R*)-(−)-myrtenal in CD_2Cl_2 and a trace of water, which leaves the (*R*)-(+)-CpMo(NO)(η^3-2-MeC_3H_4)I isomer in 45% enantiomeric excess after 77% conversion of the starting material. In addition to the organic product, an insoluble crystalline material identified by X-ray crystallography as $(\mu\text{-OH})_2[\text{CpMo(NO)I}]_2$ was formed. It crystallizes in a monoclinic cell with a space group of $P2_1/n$ with dimensions $a=10.457(1)$, $b=15.976(1)$, $c=11.076(1)$ Å, $\beta=115.989(3)°$, $V=1663.3(3)$ Å^3 and $Z=4$.

Keywords: Crystal structures; Molybdenum complexes; Nitrosyl complexes; Cyclopentadienyl complexes; Crotyl complexes; Camphorsulfonate complexes

1. Introduction

Chiral homoallylic alcohols are important organic precursors and substrates [1]. For this reason, the reaction of chiral allylmetal complexes and prochiral aldehydes to give chiral homoallylic alcohols has been widely studied [2]. It has been previously demonstrated in this laboratory that the water and air-stable halide complexes (*R*)- and (*S*)-RCpMo(NO)(η^3-allyl)X, where R = H or neomenthyl, are useful reagents for the preparation of homoallylic alcohols with high stereoselectivity and enantioselectivity [3]. These complexes have the advantage of moderate reaction rates with aldehydes at room temperature, as well as requiring no special handling techniques, which is clearly an advantage over the allylboron [4] and allyltitanium [5] systems.

The electronic asymmetry in these complexes weakens the metal–allyl bonding of the allyl terminus *trans* to the nitrosyl in these complexes leading to a facile interconversion of the η^3 and η^1 forms of the allyl [3c]. The formation of the η^1-allyl intermediate also leaves a chiral acidic site on the metal which can bind, orient and activate an aldehyde. The formation of a chair transition state accounts for the stereochemistry of the homoallylic products that are produced. Thus, the conformation for the enantiomer with the $(S)_{Mo}$ configuration at the metal leads to attack on the *re* face of



the aldehyde. For the case of the crotyl complexes shown above, the stereochemistry at the adjacent carbon is also controlled well; hence anti-alcohols are obtained [3d].

Despite their potential utility, the resolution of the molybdenum complexes, although straightforward, can be tedious. The use of the chiral neomenthylcyclopentadienyl ligand (NMCp) in lieu of Cp has been used to give the diastereomers of (+)- and (−)-NMCpMo(NO)(allyl)X, which can be resolved by fractional crystallization [3b]. These complexes have been

☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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shown to have opposite configurations at the metal and, thus, yield product alcohols of opposite chirality upon reaction with an aldehyde. We have sought alternative resolution procedures and recently described an approach [3a] where enantiomers of CpMo(NO)-(η^3-methallyl)X were resolved by conversion to diastereomers via reaction of the iodide complex with silver (*S*)-10-camphorsulfonate, AgO_3Scam^S, separation of the diastereomers via fractional crystallization and stereospecific conversion back to a halide complex with retention of configuration at the metal center. This method is not universally applicable for all CpMo(allyl) complexes, as we have been unable to separate the diastereomers formed from CpMo(NO)(η^3-allyl)X. Nevertheless, we have succeeded for the crotyl derivative (vide infra).

The technique of kinetic resolution has also been employed for the resolution of some racemic organometallic complexes. Roush and Park have resolved the diene–aldehyde iron complexes via face-selective allylboration [4a]. Baker's yeast has also been utilized to resolve similar complexes [6], including arene chromium complexes [7]. Until now, kinetic resolution has not been utilized for chiral molybdenum complexes. Two resolutions, the resolution of (±)-CpMo(NO)(η^3-*syn*-crotyl)(O_3Scam^S) and the partial kinetic resolution of (±)-CpMo(NO)(methallyl)I, as well as the crystal structures of (−)-CpMo(NO)(η^3-*syn*-crotyl)(O_3Scam^S) and $(\mu\text{-OH})_2[CpMo(NO)I]_2$, the organometallic product of the reaction of CpMo(NO)(methallyl)I and aldehydes in the presence of water, are described.

2. Results and discussion

2.1. The resolution and reactivity of η^3-syn-crotyl complexes

Racemic CpMo(NO)(η^3-crotyl)I, (±)-**1**, can be prepared in large quantity from $CpMo(CO)_2(\eta^3$-crotyl) by treatment with NO^+, and I^- [3c]. The reaction is highly stereoselective and yields the product with the nitrosyl *trans* to the methyl group of the crotyl. A mixture of the (+)- and (−)-CpMo(NO)(O_3Scam^S(η^3-crotyl) diastereomers, **2**, were produced by treatment of the iodide, (±)-**1**, with silver (*S*)-(+)-10-camphorsulfonate. The (*S*)-(−) isomer of **2** is less soluble and can be separated in high diastereomeric purity after several crystallizations.

The stereochemistry of (−)-**2** was established by single-crystal X-ray diffraction and shown to have the (*S*) absolute configuration at the metal and the methyl group of the crotyl *trans* to the nitrosyl (see Fig. 1). The methyl group was *syn* and the crotyl was in an *endo* orientation. One might note that in solution, as

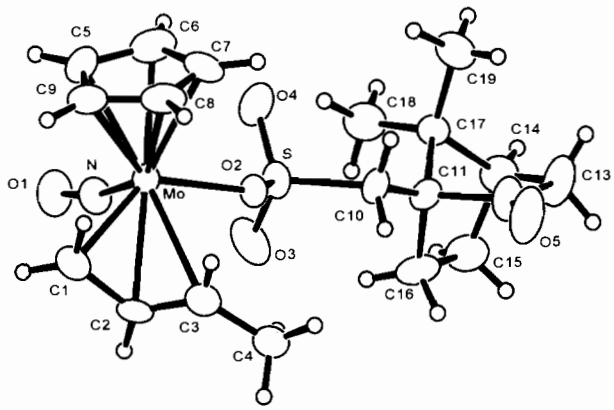


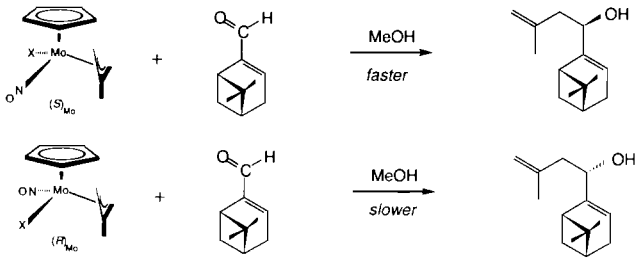
Fig. 1. ORTEP diagram of (−)-(S_{Mo})-CpMo(NO)(O_3Scam^S)(η^3-crotyl), (−)-**2**, showing 30% probability ellipsoids. Some selected bond lengths (Å) are: Mo–N 1.73(1); Mo–O2 2.12(1); Mo–C1 2.24(2); Mo–C2 2.39(2); Mo–C3 2.55(2); C1–C2 1.44(2); C2–C3 1.32(2); C3–C4 1.52(2). Selected angles (°) are: Mo–N–O1 166(1); Mo–O2–S 130.3(7); O2–Mo–N 94.8(6).

we have discussed elsewhere [3], that η^3–η^1–η^3 interconversion allows some *exo* conformation to be present in solution. Although this is not pronounced with the camphorsulfonate, both conformations (*endo*:*exo* = 3:1, $CDCl_3$) can be observed by NMR with **1**.

Using the typical test conditions described in our earlier work [3] (i.e., 0.05 mmol of molybdenum complex, 0.1 mmol of aldehyde in 0.4 ml $CDCl_3$ and 0.15 mmol methanol), (−)-NMCpMo(NO)(Cl)(η^3-crotyl) reacted with benzaldehyde to yield the (*R*,*R*)-1-phenyl-2-methylbut-2-en-1-ol in greater than 98% ee and 92% de; however, the reaction required nearly 72 h for completion. Under the same conditions (−)-**2** gave the same product in greater than 98% ee and 94% de in less than 24 h. We have generally observed that the Cp complexes react somewhat faster than the NMCp complexes and that the camphorsulfonate complexes react faster than the chlorides. The reaction times can be shortened by using methylene chloride as solvent, using more concentrated solutions and using excess aldehyde. The separation of the organometallics and side reactions can generally be improved by using water instead of methanol (vide infra).

2.2. Kinetic resolution of (±)-CpMo(NO)(η^3-2-methallyl)I

Effectively, the (*S*)-CpMo(NO)(η^3-2-methallyl)I, **3**, only reacts by attack on the *re* face of the aldehyde; whereas the (*R*) enantiomer attacks on the *si* face. With an enantiomerically pure chiral aldehyde one would expect different rates of attack on the diastereotopic faces of the aldehyde by the $(S)_{Mo}$ and $(R)_{Mo}$ complexes and, therefore, a potential kinetic resolution of the organometallic is possible. The reaction



of the chiral aldehyde myrtenal with **3** at room temperature in $CDCl_3$ and MeOH initially gave a moderate ee of 10% at 50% conversion. Changing the solvent to CD_2Cl_2 and the protonating reagent to water improved the reaction rate, the ee of the remaining organomolybdenum complex and the ease of separation of products. The enantiomeric purity was enhanced by cooling the reaction to 0 or −15 °C and gave a remaining product of 45% ee of (*R*)-(+)-**3** at 77% conversion. Under these conditions the reaction was very sluggish. What is remarkable about this chemistry is that the exceptionally long-term stability of the chiral metal center at molybdenum allows such an experiment to be performed without significant racemization of the metal center.

Consideration of the ee of the product at different percent conversions (see Table 1) allows the calculation of the relative rate constants [8] for reaction of the different enantiomers of **3** with (1R-)-(−)-myrtenal. The fact that the k_f/k_s ratio is about two indicates that the ee could almost reach above 98%, but most of the starting material would be consumed. Rate ratios above five are generally required for kinetic resolutions of really useful quantities. Enrichments of about 80% ee can be practically attained with lower ratios. Since **3** readily forms crystals, recrystallization of a fairly highly enriched sample should provide reasonable quantities of enantiomerically pure material. The only disadvantage to this technique is the fact that a large proportion of the complex will be consumed in the kinetic resolution. Fortunately, there is a facile four-step synthesis to prepare easily large quantities of (±)-**3**.

Although it is not yet practical to prepare enantiomerically pure **3** using myrtenal, one may ultimately be able to find a chiral aldehyde that would give a k_f/k_s ratio that is above five. At −15 °C, the ratio is only 1.9 for (−)-myrtenal and, according to equations relating percent conversion and final ee of substrate, one would not attain a very high ee (greater than 90%) until only about 5% of the molybdenum complex remained.

Table 1
Resolution of CpMo(NO)I(η^3-2-MeC_3H_4) with (*R*)-(−)-myrtenal

Run	Time (h)	Temp. (°C)	Conversion (%)	ee (%)
1	7	25	51	12
2	30	25	84	15
3	27	0	43	10
4	74	0	74	20
5	116	0	87	30
6	142	−15	30	12
7	408	−15	70	37
8	480	−15	77	45

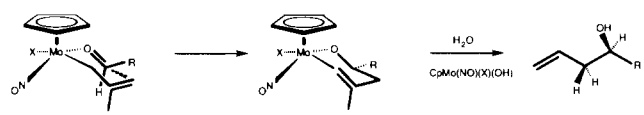
2.3. Other attempted kinetic resolutions

(*S*)-(+)-Perillaldehyde, 2,3-*O*-isopropylidene-D-glyceraldehyde and (*S*)-(+)-2-methylbutyraldehyde were also tested for selectivity in reaction with **3**. These enantiomerically pure aldehydes did react with **3**, but at 50% conversion the ee of the remaining **3** was ⩽2%.

Two other molybdenum complexes were also treated with (*R*)-(−)-myrtenal at room temperature, and they failed to give a significant ee in recovered **3**. These were the anti-crotyl iodide complex, **4**, and the allyl iodide complex **5**. These complexes reacted quite rapidly with myrtenal, but they did not give an appreciable ee at 50% conversion. The bromo and chloro analogs of **3** also failed to provide useful kinetic resolutions.

2.4. Important aspects of the mechanism of reaction

As indicated previously one expects the reaction to proceed via attack of the remote terminus of an η^1-allyl on a coordinated aldehyde. The stereochemical consequences of the chair transition state appear to be in accord with this assumption. This would then provide a coordinated alkoxide as the initial product. We have generally added another source of OH to exchange with this alkoxide and obtain the final organic product. Initially methanol was used. This was acceptable for simple aldehydes, but more hindered aldehydes react sluggishly and side reactions can occur to form less reactive hemiacetals [3a]. This can be partially overcome by using more hindered alcohols, such as 2-propanol.



We have recently found, however, that water is often the best reagent for this purpose because the organomolybdenum complex produced tends to be crystalline and relatively insoluble. On small scales, the water present in undried solvents is sufficient to hydrolyze the initial product. This allows ready separation from the other products and recovery of this crystalline cyclopentadienylmolybdenum moiety. In order to determine the identity of the organometallic product, it was analyzed by X-ray crystallography and shown to be a $[CpMo(NO)(I)(OH)]_2$ dimer with bridging hydroxyls, **6**, as shown in Fig. 2. Since a single pure side-product is produced from the molybdenum starting

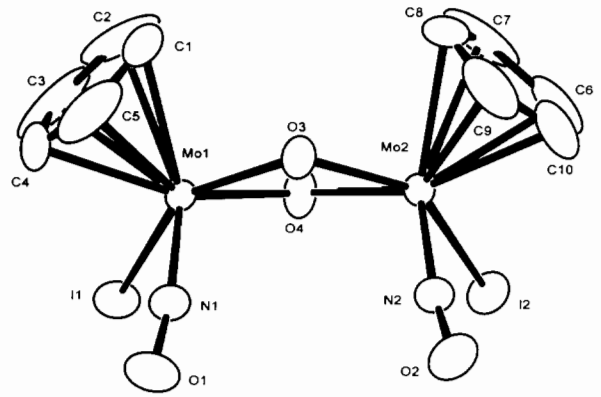


Fig. 2. ORTEP diagram of $[CpMo(NO)(I)(OH)]_2$, **6**, showing 50% probability ellipsoids. Some selected bond lengths (Å) are: Mo1–I1 2.8163(5); Mo2–I2 2.8033(5); Mo1–N1 1.763(4); Mo2–N2 1.785(4); Mo1–O3 2.104(3); Mo1–O4 2.089(3); Mo2–O3 2.108; Mo2–O4 2.090(3). Selected angles (°) are: I1–Mo1–N1 85.4(1); I2–Mo2–N2 86.6(1); O3–Mo1–O4 68.3(1); O3–Mo2–O4 68.2(1); Mo1–N1–O1 172.0(4); Mo2–N2–O2 170.9(4).

material it should be feasible to recover and recycle it.

2.5. Structural aspects

There are a number of potential isomers in a $[CpMo(NO)(I)(OH)]_2$ dimer. The isolated solid shows that the hydroxyls bridge and the cyclopentadienyl group are *cis*. There is a pseudo-mirror plane through the bridging oxygen atoms, so that it is effectively a *meso* isomer. The iodides and nitrosyls are also *cis*. The bridges are slightly puckered as indicated by the torsion angles for Mo2–O3–Mo2–O4 of 14.7(2)° and Mo1–O3–Mo2–O4 of 14.4(2)°. The bond distances and angles are unexceptional in **6**. Some selected angles are: Mo1–O3–Mo2, 109.3°; Mo1–O4–Mo2, 110.6(1)°; Mo1–N1–O1, 172.0(4)°; and Mo2–N2–O2, 170.9(4)°.

The structure of **2** was determined to establish the configuration at the metal, and the bond distances and angles found for **2** are unexceptional. One feature of note is the distortion caused by the electronic asymmetry of the other ligands on the binding of the crotyl. Thus, the Mo–C1 distance is 2.24(2) Å, whereas the Mo–C3 distance is 2.55(2) Å. This weakening of the Mo–C bond *trans* to nitrosyl accounts in large measure for the selective formation of the η^1-crotyl intermediate and the preservation of the acidic site *trans* to NO in the intermediate.

3. Experimental

(*R*)-(−)-Myrtenal, (*S*)-(+)-perillaldehyde and (*S*)-(+)-2-methylbutyraldehyde were purchased from Aldrich Chemical Co. Silver (*S*)-(+)-10-camphorsulfonate [3a] and 2,3-*O*-isopropylidene-D-glyceraldehyde [9] were prepared by literature methods. Complexes **3**, **4** and **5** were prepared as in the literature [3,10]. Enantiomeric excesses were determined by HPLC analysis using a Daicel Chiracel OD column. The solvent was n-heptane/ethanol (95:5) and the flow rate was 0.5 ml/min. The retention times were 47 min for (*R*) and 51 min for (*S*). Percent conversions were based upon isolated **1**. Identification of organic products was based on comparisons of NMR and NMR shift reagent studies discussed previously [3,11]. Under the reaction conditions of the 2-methallyl addition to myrtenal, partial dehydration of the alcohol to the polyolefin occurred.

3.1. Synthesis of (−)-CpMo(NO)(O_3Scam^S)(η^3-crotyl)·$CHCl_3$

To 2.3 mmol (0.858 g) of CpMo(NO)(I)(crotyl) in 40 ml of acetone was added 2.3 mmol (0.78 g) of silver (*S*)-(+)-10-camphorsulfonate at room temperature, under N_2, in the dark. After stirring the suspension for 15 min, it was centrifuged, filtered through a glass fiber filter and the solvent was removed under vacuum. The yield was 2.25 mmol, 98% and the diastereomeric ratio 1:1. Five crystallizations from $CHCl_3$/pentane gave 0.108 g (10%) of yellow crystals with a (−):(+) diastereomeric ratio of 98:2. From this sample, $[\alpha]^{25}_D$ −122° (c 0.2, $CHCl_3$), crystals were grown to perform an X-ray crystallographic analysis. Three more crystallizations from the same solvents did not change the ratio of diastereomers. We were unable to recover successfully the other diastereomer from the mother liquors in high enantiomeric purity.

3.2. Resolution of (−)-CpMo(NO)(O_3Scam^S)(η^3-crotyl)

Method A. CpMo(NO)(I)(crotyl) (2.03 g, 5.44 mmol) was dissolved in 40 ml of acetone and then silver (*S*)-(+)-10-camphorsulfonate (1.84 g, 5.44 mmol) was added in the dark, under N_2. The suspension was stirred for 15 min, and then centrifuged and filtered. The product was precipitated by pouring the solution into 40 ml of pentane. A yellow solid was obtained (0.92 g, 77%) with a (−):(+) diastereomeric ratio of 55:45. Four crystallizations from acetone/pentane (30:1) gave an 8% yield of a yellow solid with a (−):(+) diastereomeric ratio of 95:5, $[\alpha]^{25}_D$–116° (c 0.13 $CHCl_3$).

Method B. The same procedure was used as described in Method A, except that only 1 ml of pentane was added to the filtrate which was set aside to crystallize slowly at −15 °C. The yellow solid obtained showed a (−):(+) diastereomeric ratio of 70:30. A solid with the opposite ratio of diastereomers was obtained from the mother liquors. The former precipitate was crys-

tallized three times from acetone/pentane to obtain finally 10% of small yellow crystals with a 100% de as determined by ^{1}H NMR, $[\alpha]^{25}_D$–144° (c 0.12 $CHCl_3$). There was no spectroscopic indication of solvent incorporation, as found when chloroform was used as a solvent for crystallization.

^{1}H NMR (490 MHz, $CHCl_3$): (−)-CpMo(NO)(O_3Scam^S)(crotyl), δ 5.99 (s, Cp), 5.94–5.84 (m, H_o), 5.46–5.37 (m, H_a), 3.37 (d, $HHCSO_3$), 2.84 (d, $HHCSO_3$), 2.74–2.70 (dd, H_s), 2.69–2.61 (m, camphor), 2.44–2.99 (dd, H_a), 2.15–1.94 (m, camphor), 1.87 (d, camphor), 1.76 (s, Me camphor), 1.59–1.49 (m, camphor), 1.39–1.31 (m, camphor), 1.14 (s, Me camphor), 0.86 (Me camphor). (+)-CpMo(NO)(O_3Scam^S)(crotyl) (only the resonances which are significantly different from the (−)-diastereomer are reported), δ 5.97 (s, Cp), 3.35 (d, CH_2SO_3), 28.2 (d, CH_2SO_3), 1.88 (d, Me crotyl), 1.13 (s, Me camphor), 0.83 (s, Me camphor).

3.3. General method for kinetic resolution

Into a 5 mm NMR tube was placed (±)-**1** (34.9 mg, 0.094 mmol), and 0.60 ml of CD_2Cl_2 was added. (*R*)-(−)-Myrtenal (0.142 ml, 0.94 mmol) was added by syringe, the tube shaken and a ^{1}H NMR analysis was quickly taken. The reaction was then kept at 25, 0 or −15 °C, and ^{1}H NMR spectra were taken periodically to monitor the reaction. In all cases, a dark brown precipitate was observed and, in many cases, crystals were observed. The reaction was stopped at the appropriate time interval by opening the NMR tube, carefully decanting the soluble portion and washing the insoluble portion with CH_2Cl_2. The soluble portion was separated via silica gel thin-layer chromatography using 90:10 hexane/ethyl acetate as eluent. The red–brown band was collected to give the enantiomerically enriched **1**. The dark brown precipitate was found to be **6** by X-ray crystallographic analysis. ^{1}H NMR (300 MHz, acetone-d_6, 25 °C): δ 6.31 (s, 10H, Cp). *Anal.* Calc. for $C_{10}H_{12}I_2N_2O_4Mo_2$: C, 17.93; H, 1.81; N, 4.18. Found: C, 18.00; H, 1.78; N, 4.07%.

4. X-ray crystallographic analyses

Complete parameter sets have been forwarded to the Cambridge Crystallographic Data Center. Tables 2–4 give selected data.

4.1. (−)-CpMo(NO)(O_3Scam^S)(η^3-crotyl)·$CHCl_3$

A pale orange–yellow crystal of $MoCl_3SO_5NC_{20}H_{28}$ was mounted in a glass capillary. Monochromated Cu Kα radiation was used to provide large anomalous dispersion effects. Cell constants and an orientation matrix for data collection obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $25.14 < 2\theta < 61.29°$ corresponded to an orthorhombic cell with dimensions: $a = 7.039(1)$ Å, $b = 9.2797(6)$ Å, $c = 38.254(5)$ Å, $V = 2498.8(6)$ Å^3. For $Z = 4$ and FW = 596.80 the calculated density is 1.586 g cm^{-3}. On the basis of the systematic absences of $h00$ ($h = 2n + 1$), $0k0$ ($k = 2n + 1$), $00l$ ($l = 2n + 1$), and the successful solution and refinement of the structure, the space group was determined to be $P2_12_12_1$ (No. 19). The structure was solved by a combination of the Patterson heavy-atom method to locate the molybdenum atom and direct methods to locate the other atoms. The non-hydrogen atoms were refined anisotropically. Anomalous dispersion corrections were applied for all atoms. Hydrogen atoms were included in the full-matrix least-squares refinement at calculated positions and with isotropic thermal parameters held at $1.3 \times B_{eq}$ of the atom to which they were attached. The absolute configuration was determined by reference to the known configuration of the camphorsulfonate. The refinement converged to R and R_w values of 0.055 and 0.059, respectively. Refinement of the enantiomer gave R and R_w values of 0.061 and 0.066, respectively, which also established the correct

Table 2
Crystallographic data for X-ray diffraction studies of (−)-(S_{Mo})-CpMo(NO)(*syn*-crotyl)((S_C)-10-camphorsulfonate)·$CHCl_3$ and (μ-OH)$_2$-[CpMo(NO)I]$_2$

Crystal parameters at 23 ± 2 °C		
Formula	$MoCl_3SO_5NC_{20}H_{28}$	$Mo_2I_2O_4N_2C_{10}H_{12}$
Space group	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)
Crystal system	orthorhombic	monoclinic
a (Å)	7.039(1)	10.457(1)
b (Å)	9.280(1)	15.976(1)
c (Å)	38.254(3)	11.076(1)
β (°)	90	115.989(3)
V (Å^3)	2498.8(6)	1663.3(3)
Formula weight	596.80	669.90
ρ_{calc} (g cm^{-3})	1.586 ($Z = 4$)	2.675 ($Z = 4$)
Absolute coefficient (cm^{-1})	84.46	51.60
Crystal dimension (mm)	0.49×0.33×0.06	0.10×0.16×0.24
Intensity measurements		
Diffractometer	Rigaku AFC5S	Enraf–Nonius CAD4
Monochromator	graphite	graphite
Radiation	Cu Kα (1.54178 Å)	Mo Kα (0.71069 Å)
Reflections measured	$+h, +k, +l$	$+h, +k, \pm l$
Max. 2θ (°)	120	61
No. reflections measured	2203	5452
Solution and refinement		
Data used, $F^2 > 3\sigma(F^2)$	1411	3447
Parameters refined	280	181
Absolute correction	empirical (0.78–1.52)	psi (0.95–1.00)
p Factor	0.02	0.03
Final residuals R, R_w	0.055, 0.059	0.030, 0.040
E.s.d. of unit weight	1.72	2.04
Convergence, largest shift/error	0.00	0.03
Goodness of fit	1.72	1.47
Largest $\Delta(\rho)$ (e Å^{-3})	0.54	0.99

Table 3
Fractional atomic coordinates and B_{eq} for (−)-CpMo(NO)-(crotyl)(camphorsulfonate), (−)-**2**

Atom	x	y	z	B_{eq}
Mo	−0.0097(2)	0.0345(1)	0.05422(3)	3.08(5)
Cl1	0.763(1)	0.1060(6)	0.2086(2)	7.5(4)
Cl2	1.028(2)	0.241(1)	0.2520(2)	15.5(7)
Cl3	1.158(1)	0.0782(7)	0.1943(2)	11.5(6)
S	0.2812(7)	−0.1669(5)	0.0995(1)	3.9(2)
O1	0.361(2)	0.101(1)	0.0215(3)	5.8(8)
O2	0.088(2)	−0.132(1)	0.0876(3)	3.8(6)
O3	0.396(2)	−0.223(2)	0.0726(3)	6.6(8)
O4	0.368(2)	−0.047(1)	0.1174(3)	6.5(8)
O5	0.130(2)	−0.533(2)	0.1723(4)	7.5(9)
N	0.205(2)	0.057(2)	0.0331(4)	3.7(7)
C1	−0.162(3)	0.030(2)	0.0027(5)	5(1)
C2	−0.113(3)	−0.120(2)	0.0080(4)	5(1)
C3	−0.188(3)	−0.190(2)	0.0346(5)	6(1)
C4	−0.129(3)	−0.342(2)	0.0449(4)	5(1)
C5	−0.024(5)	0.275(2)	0.0673(5)	7(1)
C6	0.025(4)	0.199(2)	0.0994(5)	6(1)
C7	−0.139(3)	0.119(2)	0.1068(5)	5(1)
C8	−0.280(3)	0.140(2)	0.0836(6)	5(1)
C9	−0.212(3)	0.236(2)	0.0587(5)	5(1)
C10	0.231(3)	−0.303(2)	0.1307(5)	4(1)
C11	0.388(3)	−0.397(2)	0.1456(5)	4(1)
C12	0.299(3)	−0.500(2)	0.1725(6)	5(1)
C13	0.450(3)	−0.560(2)	0.1942(5)	5(1)
C14	0.618(3)	−0.490(2)	0.1778(6)	5(1)
C15	0.659(4)	−0.556(2)	0.1436(5)	7(1)
C16	0.499(3)	−0.496(2)	0.1202(5)	5(1)
C17	0.549(2)	−0.334(2)	0.1696(4)	3(1)
C18	0.690(3)	−0.244(2)	0.1494(5)	6(1)
C19	0.473(3)	−0.247(2)	0.2002(4)	5(1)
C20	0.985(4)	0.188(2)	0.2102(5)	7(1)

Table 4
Fractional atomic coordinates and B_{eq} for [CpMo(NO)(I)(OH)]$_2$, **6**

Atom	x	y	z	B_{eq}
I1	−0.00482(4)	0.11960(2)	−0.14684(4)	4.13(1)
I2	−0.10943(4)	0.12656(2)	0.28515(4)	4.14(1)
Mo1	0.24788(4)	0.15274(2)	0.08569(4)	2.39(1)
Mo2	0.18048(4)	0.15535(2)	0.36268(4)	2.53(1)
O1	0.1912(5)	0.3301(2)	0.0077(5)	5.3(2)
O2	0.1239(5)	0.3345(2)	0.3685(5)	5.1(2)
O3	0.3339(4)	0.1803(2)	0.2921(3)	3.3(1)
O4	0.1248(4)	0.1022(2)	0.1738(4)	3.6(1)
N1	0.2077(4)	0.2591(3)	0.0436(4)	3.4(2)
N2	0.1397(4)	0.2643(3)	0.3551(4)	3.4(2)
C1	0.477(1)	0.095(1)	0.1718(8)	8.9(5)
C2	0.394(2)	0.0340(6)	0.095(2)	12.5(8)
C3	0.334(1)	0.063(1)	−0.030(2)	10.8(7)
C4	0.377(1)	0.137(1)	−0.032(1)	9.1(6)
C5	0.467(1)	0.1591(6)	0.093(2)	8.2(5)
C6	0.1906(9)	0.0847(7)	0.5532(8)	7.4(4)
C7	0.266(2)	0.0318(4)	0.4990(8)	10.8(5)
C8	0.382(1)	0.0849(8)	0.518(1)	8.4(5)
C9	0.370(1)	0.1556(8)	0.5683(9)	8.5(5)
C10	0.261(1)	0.1560(6)	0.5920(7)	7.4(4)

enantiomorph. Other relevant data are given in Table 1.

4.2. *[CpMo(NO)(I)(OH)]$_2$*

A red–brown plate of $C_{10}H_{12}N_2O_4I_2Mo_2$ was mounted on a glass fiber. Measurements were made on an Enraf–Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation. Cell constants and an orientation matrix for data collection obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $15.00 < 2\theta < 40.00°$ corresponded to a monoclinic cell with dimensions: $a = 10.457(1)$ Å, $b = 15.976(1)$ Å, $c = 11.076(1)$ Å, $\beta = 115.989(3)°$ and $V = 1663.3(3)$ Å^3. For $Z = 4$ and FW = 669.90 the calculated density is 2.675 g/cm^3. On the basis of the systematic absences of $h0l$ ($h + 1 = 2n + 1$), $0k0$ ($k = 2n + 1$), and the successful solution and refinement of the structure, the space group was determined to be $P2_1/n$ (No. 14). Other relevant data are given in Table 1.

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