Synthesis and Coordination of the New Chiral Tridentate O,N,O Ligand 2,6-Bis[(1*S*,2*S*,5*R*)-(−)-menthyl]pyridine to Molybdenum(VI) and Vanadium(V) Oxo Complexes: Crystal Structures of [(2,6-Bis{(−)-menthyl}pyridine)MoO_2] and [(2,6-Bis{(−)-menthyl}pyridine)VO$]_2$(μ-O)

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Keywords: Molybdenum / Vanadium / Chiral ligands / Oxo complexes / Homogeneous catalysis

The novel tridentate chiral ligand 2,6-bis{(–)-menthyl}-pyridine (**1**), was readily prepared from the reaction of 2,6-dilithiopyridine with (–)-menthone. Reaction of **1** with VO(O*i*Pr$)_3$ and [MoO_2(acac$)_2$] resulted in the formation of the new metal-oxo complexes [VO(ONO)$]_2$(μ-O) (**2**) and [MoO_2(ONO)] (**3**) [ONO = (**1** – 2 H)]. Both metal-oxo compounds **2** and **3** have demonstrated the ability to catalyze the asymmetric oxidation of prochiral olefins with *t*BuOOH as the oxidant. The compounds **1**–**3** have been fully characterized by ^{1}H, ^{13}C and ^{51}V (where appropriate) NMR spectroscopy, mass spectrometry, microanalysis and IR spectroscopy. Furthermore, the molecular structures of **2** and **3** have been determined by single-crystal X-ray diffraction.

Introduction

Vanadium(V) and molybdenum(VI) compounds[1,2] are of great importance in catalytic reactions involving oxidation processes. Nature makes use of both of these metal centers in oxidation reactions, for example in vanadium bromoperoxidases[3] and molybdenum oxotransferase enzymes.[4] Our interest in this area lies mainly in the development of new asymmetric oxidation catalysts[5,6] using novel tridentate chiral ligands possessing nitrogen and oxygen donor atoms. It has previously been demonstrated that asymmetric tridentate bis-alkoxy nitrogen donor ligands can be used in epoxidation reactions,[7,8] as well as oxo transfer reactions to sulfides,[9] with peroxides as the co-oxidant. However, in the former case, selectivity appears to be lower than in other known systems, while in the latter, the nature of the catalytically active species remains uncertain. Dioxomolybdenum(VI) complexes containing achiral pyridine alkoxy ligands have also been shown to have great potential in the oxidation of terminal olefins with molecular oxygen.[10,11] Herein we describe the synthesis of the novel tridentate chiral ligand 2,6-bis{(−)-menthyl}pyridine (**1**) and its coordination to vanadium and molybdenum to give the new asymmetric oxo complexes [VO(ONO)$]_2$(μ-O) **(2)** and [MoO_2(ONO)] **(3)** {ONO = 2,6-bis{(−)-menthyl}-pyridine}. The molecular structures of **2** and **3** are presented and their potential as asymmetric epoxidation catalysts discussed.

Results and Discussion

The new chiral ligand 2,6-bis{(−)-menthyl}pyridine (**1**), characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry and microanalysis, is readily prepared by the reaction of 2,6-dilithiopyridine with (−)-menthone. Reaction of the chiral pyridine-diol ligand **1** with VO(O*i*Pr$)_3$ or MO_2(acac$)_2$ resulted in displacement of the weakly coordinated O*i*Pr or acac ligands to give the corresponding vanadium(V) and molybdenum(VI) oxo complexes [VO(ONO)$]_2$(μ-O) **(2)** and [MoO_2(ONO)] **(3)** {ONO = 2,6-bis{(−)-menthyl}pyridine} in high yield (Scheme 1).

It was evident from the ^{1}H and ^{13}C NMR spectroscopic data that coordination of the C_2 symmetric ligand **1** to vanadium, to give complex **2**, resulted in two nonequivalent menthol moieties. Crystallographic analysis of a suitable crystal showed the complex to be dimeric in the solid state. The molecular structure of **2**·C_6H_{12} is shown in Figure 1 and the selected bond lengths and bond angles are given in Table 1. Two five-coordinate vanadium atoms are bridged by an oxygen atom to form the binuclear asymmetric unit of the cell. The binuclear unit of **2** appears to be somewhat unique when compared to other V^V-V^V dimeric oxo complexes[12−14] as the two independent V atoms, V(1) and V(2), contain different coordination geometries. V(1) appears to possess a slightly distorted square pyramidal arrangement of ligands with the oxo ligand in the apical position and the metal center displaced 0.40 Å above the equatorial plane. However, V(2) is best approximated by a trigonal bipyramidal arrangement with the oxo and bridging oxo ligand in the equatorial plane (Figure 1). However, one could argue that V(1) is simply a more distorted trigonal bipyramidal arrangement of ligands than V(2). The V=O distances [V(1)−O(2) = 1.575(5) Å, V(2)−O(5) = 1.600(5) Å]

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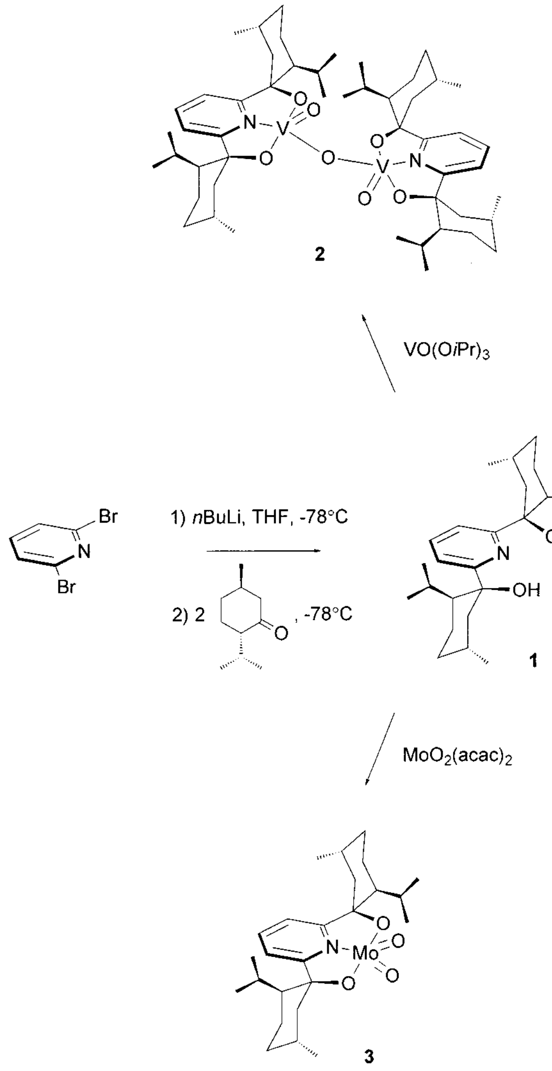

Scheme 1. Synthesis of complexes **2** and **3**.

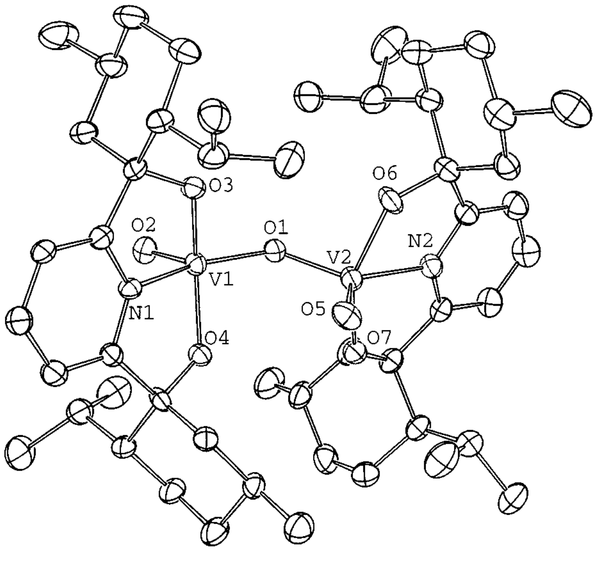

Figure 1. Molecular structure of [(2,6-Bis{(−)-menthyl}pyridine)-VO]$_2$(μ-O)·C_6H_{12} (**2**).

Table 1. Selected bond lengths (Å) and angles (deg) for **2**·C_6H_{12} and **3**·C_6H_{14}

2·C_6H_{12}		**3**·C_6H_{14}	
Bond Lengths			
V(1)−O(1)	1.810(4)	Mo(1)−O(1)	1.763(7)
V(1)−O(2)	1.575(5)	Mo(1)−O(2)	2.438(9)
V(1)−O(3)	1.834(4)	Mo(1)−O(3)	1.694(9)
V(1)−O(4)	1.845(4)	Mo(1)−O(4)	1.911(7)
V(1)−N(1)	2.056(5)	Mo(1)−O(5)	1.916(8)
V(2)−O(1)	1.770(4)	Mo(1)−N(1)	2.17(1)
V(2)−O(5)	1.600(5)	Mo(2)−O(1)	2.426(8)
V(2)−O(6)	1.846(5)	Mo(2)−O(2)	1.754(7)
V(2)−O(7)	1.836(5)	Mo(2)−O(6)	1.692(8)
V(2)−N(2)	2.104(6)	Mo(2)−O(7)	1.924(7)
		Mo(2)−O(8)	1.908(8)
		Mo(2)−N(2)	2.187(9)
Bond Angles			
O(1)−V(1)−N(1)	152.7(2)	O(1)−Mo(1)−O(2)	73.6(3)
O(1)−V(1)−O(2)	107.7(2)	O(1)−Mo(1)−O(3)	105.5(4)
O(1)−V(1)−O(3)	97.0(2)	O(1)−Mo(1)−O(4)	105.6(4)
O(1)−V(1)−O(4)	97.2(2)	O(1)−Mo(1)−O(5)	99.9(4)
N(1)−V(1)−O(2)	99.5(2)	O(1)−Mo(1)−N(1)	155.6(4)
O(2)−V(1)−O(3)	104.0(2)	O(2)−Mo(1)−O(3)	177.4(4)
O(2)−V(1)−O(4)	104.6(2)	O(2)−Mo(1)−O(4)	79.5(3)
V(1)−O(1)−V(2)	128.2(3)	O(2)−Mo(1)−O(5)	82.8(3)
O(1)−V(2)−N(2)	121.5(2)	O(2)−Mo(1)−N(1)	82.3(3)
O(1)−V(2)−O(5)	109.6(2)	O(3)−Mo(1)−O(4)	98.5(4)
O(1)−V(2)−O(6)	100.9(2)	O(3)−Mo(1)−O(5)	98.8(5)
O(1)−V(2)−O(7)	99.3(2)	O(3)−Mo(1)−N(1)	98.7(4)
N(2)−V(2)−O(5)	128.8(2)	O(4)−Mo(1)−O(5)	143.1(4)
O(5)−V(2)−O(6)	98.0(2)	O(4)−Mo(1)−N(1)	72.9(4)
O(5)−V(2)−O(7)	96.6(2)	Mo(1)−O(1)−Mo(2)	105.9(3)
O(6)−V(2)−O(7)	149.3(2)	Mo(1)−O(2)−Mo(2)	105.7(3)

are characteristic of a double bond; however, the difference between the two values is intriguing and may be a consequence of the different coordination geometries of the two metal centers. The bridging oxo bond is unsymmetrical with V(1)−O(1) = 1.810(4) Å and V(2)−O(1) = 1.770(4) Å and the V(1)−O1−V(2) angle is 128.3(3)°, a rare example of a complex having a V−O−V angle near to 120°.[12] The two terminal oxygen atoms are *trans*-directed lying on opposite sides of the VOV plane (Figure 1). The remaining ligand-to-metal bonds are unexceptional.

The ^{1}H and ^{13}C NMR spectra of **3** showed, as expected, one set of resonances for the two menthol groups on the chiral pyridine-diol ligand suggesting the formation of a C_2-symmetric five-coordinate molybdenum dioxo complex. This was confirmed by solution IR spectroscopy which showed two sharp bands of equal intensity at 938 and 918 cm^{-1} for the symmetric and asymmetric stretch of the molybdenum-dioxo unit. However, interestingly, the IR spectrum in the solid state suggests that the molybdenum complex is oligomeric as no sharp or clear Mo=O stretches are observed. This was confirmed by a crystallographic analysis of a suitable crystal of **3**·C_6H_{14}, which revealed two independent five-coordinate mononuclear complexes that are weakly associated by two Mo=O···Mo interactions to give an essentially "binuclear" structure. The molecular structure of **3**·C_6H_{14} is shown in Figure 2, and selected bond lengths and bond angles are given in Table 1. A sim-

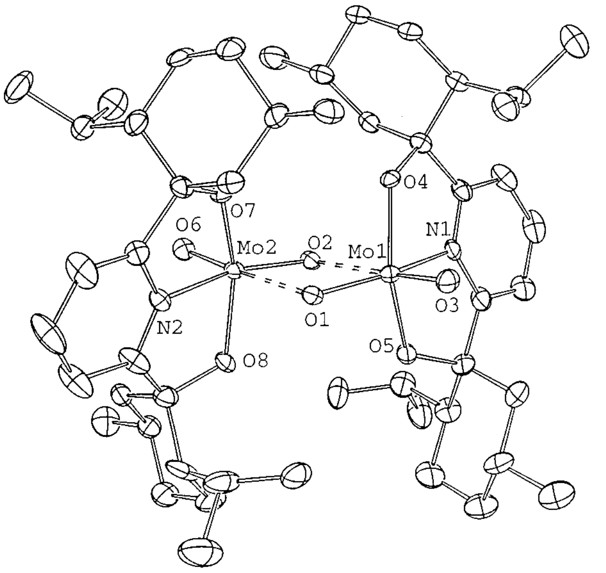

Figure 2. Molecular structure of [(2,6-Bis{(−)-menthyl}pyridine)-MoO_2]·C_6H_{14} (**3**).

ilar interaction can be seen in the structure of $[MoO_2(C_5H_3N\text{-}2,6\text{-}(CH_2O)_2)]_n$[15] where the Mo=O···Mo interaction in this case leads to a "linear" polymeric structure, with the sixth site in the distorted octahedral coordination sphere occupied by an oxo atom of an adjacent molecule. The "dimer" formation of **3** in the solid state provides a new structural type for dioxomolybdenum(VI) complexes. Typically, five-coordinate dioxomolybdenum(VI) complexes have been found to be monomeric[7,16] or polymeric.[15] Complex **3** has a distorted octahedral stereochemistry containing *cis*-oxo groups with the Mo=O unit of the second molecule *trans* to the oxo group. The terminal Mo=O distances [1.694(9) Å, 1.692(8) Å] are similar to other known Mo=O distances.[17] The Mo=O moiety that is found to interact with the second metal center is slightly longer [1.763(7) Å, 1.754(7) Å] than the other Mo=O bond lengths;[17] however, the distances are still short enough to suggest that the Mo=O bond retains much of its double bond character. The Mo···O interactions [2.438(9) Å, 2.426(8) Å] are too large to be considered a formal bond, but are in line with the Mo···O=Mo distance found in the polymeric complex $[MoO_2(C_5H_3N\text{-}2,6\text{-}(CH_2O)_2)]_n$ (2.518(3) Å). However, the Mo···O=Mo angles in **3** [105.88(3)°, 105.72(3)°] are considerably smaller than in the polymeric structure [151.7(2)°].[15] The remaining chiral pyridine-diol ligand bonds to the molybdenum center are unexceptional.

Conclusion

We have demonstrated the facile two-step synthesis of a new, inexpensive, chiral pyridine-diol ligand **1** and its coordination to both V^V and Mo^{VI} metal centers to form the metal oxo complexes **2** and **3**. Preliminary studies show that both complexes **2** and **3** (1 mol-%) are active in the catalytic asymmetric epoxidation of 1-hexene in conjunction with *t*BuOOH: 50% conversion into the epoxide has been observed for both metal complexes with an enantiomeric excess of up to 25%. Further work is underway to optimize the selectivity of this reaction and to test the versatility of complexes **2** and **3**. The coordination properties of the asymmetric ligand **1** to other metal centers will also be investigated further.

Experimental Section

General Remarks: Unless otherwise specified, all reagents were purchased from commercial suppliers and used without purification. All experiments were carried out using dried solvents and under a nitrogen or argon atmosphere, using a Schlenk line or a Vacuum Atmospheres glovebox equipped with a Dri-Train HE-493 inert atmosphere purifier. − ^1H (300 MHz) and $^{13}C\{^1H\}$ (75 MHz) NMR spectra were recorded on a Bruker AC300 NMR spectrometer and referenced to Me_4Si; ^{51}V (105 MHz) NMR spectra were recorded on a Bruker AM400 NMR spectrometer and referenced to $VOCl_3$. − FTIR spectra were recorded using a Perkin−Elmer Model FTIR-1600 spectrometer on KBr discs. − Mass spectrometry and elemental analyses were carried out by the corresponding facilities at the Chemistry Research Center at the Université Louis Pasteur, Strasbourg.

Synthesis of 2,6-Bis{(−)-menthyl}pyridine (1): To a solution of *n*BuLi (69.0 mmol, 43.50 mL, 1.6 M in hexane) in 100 mL of THF was added dropwise a solution of 2,6-dibromopyridine (7.50 g, 31.5 mmol) in 50 mL of THF at −100 °C. After 1 hour at −100 °C and 3 hours at −78 °C, a solution of (−)-menthone (11.55 g, 75.0 mmol) in 25 mL of THF was added slowly. The mixture was then left to warm to room temperature overnight. Distilled water (500 mL) was then added and the organic phase extracted with 2 × 150 mL of diethyl ether. The collected organic phases were washed with a solution of $NaHCO_3$, dried over $MgSO_4$ and the solvents removed under vacuum to afford a yellow oil. This yellow oil was purified by the preparation of the pyridinium salt by reaction with the resolving agent D-(1*S*)-(+)-camphor-10-sulfonic acid. Thus, a solution of D-(1*S*)-(+)-camphor-10-sulfonic acid (7.31 g, 31.5 mmol) in 100 mL of acetonitrile was added to the yellow oil. After reduction of the volume to 40 mL, 250 mL of diethyl ether was added. The flask was then cooled to −25 °C and colorless crystals formed overnight. The crystals were collected, washed with cold diethyl ether and dried under vacuum (8.80 g). Finally, the crystals were dissolved in CH_2Cl_2 and washed with an aqueous solution of $NaHCO_3$. The solution was then dried over $CaSO_4$ and the solvent removed to afford **1** as a colorless oil (4.0 g, 30%), which was shown to be optically pure by chiral HPLC (Chiralcel OD column). − ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.66$ [d, $^3J = 6.9$ Hz, 6 H, CH_3 (menthone)], 0.81 [d, $^3J = 6.8$ Hz, 6 H, CH_3 (ment.)], 0.90 [d, $^3J = 6.4$ Hz, 6 H, CH_3 (ment.)], 0.95−1.30 [m, 4 H, CH_2 (ment.)], 1.40−2.00 [m, 16 H, CH, CH_2 (ment.)], 4.2 (very broad, OH), 7.33 [d, $^3J = 7.8$ Hz, 2 H, CH (arom.)], 7.70 [t, $^3J = 7.8$ Hz, 1 H, CH (arom.)]. − $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 18.5$ [2 CH_3 (ment.)], 21.6 [2 CH_2 (ment.)], 22.2 [2 CH (ment.)], 23.4 [2 CH (ment.)], 27.2 [2 CH_3 (ment.)], 28.4 [2 CH_3 (ment.)], 35.1 [2 CH_2 (ment.)], 50.0 [2 CH_2 (ment.)], 49.6 [2 CH (ment.)], 78.0 (2 C−OH), 117.1 [2 C (arom.)], 137.4 [C (arom.)], 163.7 [2 C (arom.)]. − IR (KBr): $\tilde{\nu} = 3462$ (s br), 2952 (s), 2868 (s), 1580 (w), 1577 (m), 1456 (s), 1386 (m), 1366 (m), 1294 (w), 1264 (w), 1165 (m), 1160 (m), 1094 (w), 1058 (m), 1023 (w), 978 (w), 948 (m), 910 (w), 891 (w), 852 (w), 807 (m), 756 (m), 714 (w), 671 (w), 641 (w), 516 (w) cm^{-1}. − MS (EI +): $m/z = 387.3$ [M^+]. − $C_{25}H_{41}NO_2$ (387.61): calcd. C 77.47, H 10.66, N 3.61; found C 77.36, H 10.45, N 3.62.

Synthesis of [(2,6-Bis{(−)-menthyl}pyridine)VO]$_2$(μ-O) (2): Ligand **1** (0.120 g, 0.31 mmol) was dissolved in CH_2Cl_2 (5 mL), treated with [VO(O*i*Pr)$_3$] (0.073 g, 0.30 mmol) and stirred for 2 hours at room temperature. The solvent was then removed under vacuum and the resulting solid redissolved in ether (3 mL). Distilled water (5 μL) was then added and the solution left to crystallize overnight at 4 °C. The resulting yellow crystals were collected and dried under vacuum (120 mg, 86%). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.73 [d, ^3J = 6.9 Hz, 6 H, CH_3 (menthone)], 0.81 [d, ^3J = 6.9 Hz, 6 H, CH_3 (ment.)], 0.87 [d, ^3J = 6.7 Hz, 6 H, CH_3 (ment.)], 0.90 [d, ^3J = 6.6 Hz, 6 H, $-CH_3$ (ment.)], 1.09 [d, ^3J = 6.8 Hz, 12 H, CH_3 (ment.)], 1.20−2.20 [m, 30 H, CH_2, CH (ment.)], 2.65 [m, 2 H, CH (ment.)], 7.14 [d, ^3J = 7.6 Hz, 2 H, CH (arom.)], 7.16 [d, ^3J = 7.7 Hz, 2 H, CH (arom.)], 7.88 (dd, ^3J = 7.7 Hz 2 H, CH (arom.)]. − ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 19.0 [CH_3 (ment.)], 19.4 [CH_3 (ment.)], 21.4 [CH_2 (ment.)], 22.0 [CH_2 (ment.)], 22.4 [CH (ment.)], 22.7 [CH (ment.)], 23.9 [CH (ment.)], 24.2 (CH (ment.)], 28.3 [CH_3 (ment.)], 35.5 [CH_2 (ment.)], 50.7 [CH_2 (ment.)], 51.7 [CH (ment.)], 99.2 [C (ment.)], 99.7 [C (ment.)], 117.0 [CH (arom.)], 117.3 [CH (arom.)], 141.6 [CH (arom.)], 175.7 [C (arom.)]. − ^{51}V NMR (105 MHz, $CDCl_3$): δ = −533 ($\nu_{1/2}$ = 163 Hz). − IR (KBr): ṽ = 3069 (w), 2949 (s br), 2865 (s br), 1600 (m), 1579 (m), 1466 (s), 1384 (w), 1365 (w) 1296 (m), 1205 (w), 1144 (w), 1057 (w), 976 (s), 949 (s), 900 (w), 864 (w), 808 (m), 761 (s), 714 (s), 596 (m), 530 (m), 516 (m) cm^{-1}. − MS (CI (−)]: *m*/*z* (%) = 469.3 (100) 1/2 [M + H]$^-$. − $C_{50}H_{78}N_2O_7V_2$ (921.05): calcd. C 65.20, H 8.54; found C 66.11, H 8.48.

Synthesis of [(2,6-Bis{(−)-menthyl}pyridine)MoO$_2$] (3): [MoO$_2$(acac)$_2$] (0.820 g, 2.51 mmol) was dissolved in MeOH (40 mL) and treated with ligand **1** (1.00 g, 2.58 mmol). The solution was then refluxed for 30 mins and, upon cooling, a white precipitate was formed. The reaction mixture was filtered and the white solid dried in vacuo (0.900 g, 70%). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.78 [d, ^3J = 6.8 Hz, 6 H, CH_3 (menthone)], 0.93 [d, ^3J = 6.3 Hz, 6 H, CH_3 (ment.)], 0.95 [d, ^3J = 6.7 Hz, 6 H, CH_3 (ment.)], 1.01−2.01 [m, 18 H, CH_2, CH (ment.)], 7.34 [d, ^3J = 7.7 Hz, 2 H, CH (arom.)], 8.14 (dd, ^3J = 7.7 Hz, 1 H, CH (arom.)]. − ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 18.9 [CH_3 (ment.)], 21.8 [CH_2 (ment.)], 22.1 [CH (ment.)], 23.9 [CH (ment.)], 28.4 [CH_3 (ment.)], 34.9 [CH_2 (ment.)], 50.1 [CH_2 (ment.)], 51.1 [CH (ment.)], 98.9 [C (ment.)], 118.4 [CH (arom.)], 143.7 [CH (arom.)], 173.3 [C (arom.)]. − IR (KBr): ṽ = 3071 (w), 2950 (s br), 1605 (m), 1578 (m), 1469 (s), 1384 (m), 1363 (m), 1297 (s), 1205 (m), 1173 (m), 1145 (m), 1106 (w), 1093 (w), 1062 (s), 1030 (m) 1010 (m), 978 (s), 936 (s br), 860 (s), 835 (m), 802 (m), 759 (m), 708 (s), 674 (w), 626 (w), 588 (m), 552 (m), 515 (s), 478 (m), 373 (w) cm^{-1}. − IR (CH_2Cl_2): ṽ = 938 ($\nu_{(Mo=O)}$, symmetric), 918 ($\nu_{(Mo=O)}$, asymmetric) cm^{-1}. − MS (EI +): *m*/*z* = 515.2 [M$^+$]. − $C_{25}H_{39}MoNO_4$ (513.52): calcd. C, 58.47, H 7.65, N 2.73; found C 58.53, H 7.77, N 2.89.

Table 2. Crystal data and summary of intensity data collection and structure refinement of **2**·C_6H_{12} and **3**·C_6H_{14}

Emperical formula	**2**·C_6H_{12} $C_{50}H_{78}N_2O_7V_2 \cdot C_6H_{12}$	**3**·C_6H_{14} $C_{50}H_{78}N_2O_8Mo_2 \cdot C_6H_{14}$
fw	1005.23	1113.25
space group	$P2_1$	$P2_12_12_1$
a/Å	13.091(1)	14.026(1)
b/Å	15.574(1)	16.512(1)
c/Å	15.019(1)	24.694(1)
α/°	90	90
β/°	111.54(1)	90
γ/°	90	90
V/Å^3	2848.2(3)	5719.0(8)
Z	2	4
ρcalc/g cm^{-3}	1.17	1.29
μ/mm^{-1}	0.363	0.476
diffractometer	KappaCCD	KappaCCD
T/K	173	173
scan type	phi scans	phi scans
no. of data meas.	21383	25775
no. of data used	3469	3359
criterion	$I > 3\sigma(I)$	$I > 3\sigma(I)$
no. of variables	603	613
R[a]	0.041	0.050
R_w[b]	0.061	0.074
Flack × param	0.08(3)	0.03(7)
largest peak (eÅ^{-3})	0.400	0.486
GOF[c]	1.221	1.048

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. − [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o{}^2)]^{1/2}$. − [c] GOF $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$.

X-ray Crystallographic Study: The oxo complexes **2**·C_6H_{12} and **3**·C_6H_{14} were crystallized by slow diffusion of cyclohexane and hexane, respectively, layered onto a solution of the complex in dichloromethane. The intensity data were obtained at 173 K with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) on a Nonius Kappa CCD diffractometer. The structures were solved using direct methods and refined against |*F*|. Hydrogen atoms were introduced as fixed contributors. For all computations the Enraf−Nonius MolEN package was used.[18] Additional data collection and refinement parameters are presented in Table 2.[19] The absolute configuration of each compound was determined and confirmed: Flack parameters were 0.08(3) for **2**·C_6H_{12} and 0.03(7) for **3**·C_6H_{14}.

Acknowledgments

We gratefully acknowledge the support of this work by the Centre National de la Recherche Scientifique and we would like to thank Nathalie Gruber, Dr. André De Cian and Prof. Jean Fischer for X-ray analyses and Dr. Marie-Thérèse Youinou for helpful discussions. K. S. C. also wishes to thank the European Commission and P. D. the Deutsche Forschungsgemeinschaft for their support.

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[19] Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-137162 (**2**·C_6H_{12}) and -137163 (**3**·C_6H_{14}). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Received December 30, 1999
[I99476]