Dioxomolybdenum(VI) Complexes with New Enantiomerically Pure Amino Diol Ligands

Pierluigi Barbaro,* Tomás R. Belderrain, Claudio Bianchini,*,† Giancarlo Scapacci, and Dante Masi

Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione del CNR, Via J. Nardi 39, 50132 Firenze, Italy

(*R*)-Phenylglycinol is shown to be an efficient building block for the synthesis of chiral amino diols in pure diastereomeric form by epoxide ring-opening reactions. The reaction with *rac-trans*-stilbene oxide gives [HOCH₂-(*R*)-PhCH]NH[(*S*)-PhCH-(*R*)-PhCHOH] [2(*R*)-3(*R*)-4(*S*)-HNO₂H₂] in 32% yield, which can be methylated at nitrogen to give enantiomerically pure [HOCH₂-(*R*)-PhCH]NCH₃[(*S*)-PhCH-(*R*)-PhCHOH] [2(*R*)-3(*R*)-4(*S*)-MeNO₂H₂]. These amino diol ligands have been used to prepare chiral dioxomolybdenyl complexes of the formula *N*(*R*)-2(*R*)-3(*R*)-4(*S*)-(HNO₂)MoO₂ (**1**) and *N*(*R*)-2(*R*)-3(*R*)-4(*S*)-(MeNO₂)MoO₂ (**2**). The absolute configuration at each stereocenter in the Mo(VI) complexes has been established by ¹H NOESY spectroscopy. The configuration determined for **1** has been confirmed by an X-ray analysis. Crystal data: orthorhombic $P2_12_12_1$, $a = 7.620(3)$, $b = 13.589(2)$, $c = 20.339(3)$ Å, $Z = 4$, $R = 0.0336$. The structure consists of a polymeric chain of *N*(*R*)-2(*R*)-3(*R*)-4(*S*)-(HNO₂)MoO₂ molecules connected through unsymmetrical Mo=O → Mo bridges. Each metal center is coordinated in a distorted octahedral geometry by a *cis* dioxo unit and by two *trans* alkoxo atoms. The coordination polyhedron is completed by a nitrogen atom and by a bridging oxo oxygen atom from an adjacent molecule. Compound **2** catalyzes the oxidation of PPh₃ to OPPh₃ by DMSO through a mechanism that involves the intermediacy of a Mo(IV) species.

Introduction

The synthesis of chiral tridentate ligands is a topic of much interest due to the current need to develop enantiomerically pure metal catalysts with unique characteristics of chemo- and stereoselectivity.[1] Among the various donor-atom sets, those comprising nitrogen and oxygen are particularly suited for the formation of active catalysts in conjunction with Lewis-acid metal ions derived from molybdenum, vanadium, titanium, aluminum, or boron.[2] However, only a few examples of tridentate chiral amino diols have been reported so far.[3]

In this paper we describe the synthesis and the characterization of two novel tridentate diastereomerically pure amino diols containing three asymmetric centers. These ligands have appropriately been designed to obtain chiral dioxomolybdenum-

(VI) complexes of which few examples are known despite their potential in asymmetric oxidation reactions.[4] The steric hindrance of the ligands described in this paper has purposely been tailored to avoid the dimerization to Mo(V) species, which often represents an obstacle to the use of dioxomolybdenum(VI) complexes in oxo-transfer reactions.[5]

Experimental Section

Materials and Methods. Unless otherwise stated, all the manipulations were performed under a pure nitrogen atmosphere. MoO₂(acac)₂ and (*R*)-(−)-phenylglycinol were purchased from Aldrich. *trans*-Stilbene oxide was synthesized by use of published methods.[6] Diethyl ether and *n*-heptane were distilled from sodium, while DMSO and DMF were dried over 4 Å molecular sieves. All the other chemicals were commercial products and were used as received without further purification. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer using samples mulled in Nujol between KBr plates. Optical rotations were measured with a Perkin-Elmer 341 polarimeter using 10 cm cells. The ¹H and ¹³C NMR spectra were recorded at 298 K on a Bruker Avance DRX-500 spectrometer operating at 500.132 and 125.77 MHz, respectively, and equipped with a variable temperature control unit accurate to ±0.1 °C. Chemical shifts are relative to tetramethylsilane. The assignments of the signals resulted

† E-mail: bianchin@cacao.issecc.fi.cnr.it.
⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1996.

(1) (a) Barbaro, P.; Togni, A. *Organometallics* **1995**, *14*, 3570. (b) Brunner, H.; Reiter, B.; Riepl, G. *Chem. Ber.* **1968**, *90*, 522. (c) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1975**, *85*, 19. (d) Johnson, T.; Klein, K.; Thomen, S. *J. Mol. Catal.* **1981**, *12*, 37. (e) Togni, A.; Pastor, S. D. *J. Org. Chem.* **1990**, *55*, 1649. (f) Bianchini, C.; Farnetti, E.; Glendenning, L.; Graziani, M.; Nardin, G.; Peruzzini, M.; Rocchini, E.; Zanobini, F. *Organometallics* **1995**, *14*, 1489. (g) Burk, M. J.; Harlow, R. L. *Angew. Chem.* **1990**, *102*, 1511. (h) Burk, M. J.; Feaster, J. E.; Harlow, R. L. *Tetrahedron: Asymmetry* **1991**, *2*, 569. (i) Ward, T. R.; Venanzi, L. M.; Albinati, A.; Lianza, F.; Gerfin, T.; Gramlich, V.; Ramos Tombo, G. M. *Helv. Chim. Acta* **1991**, *74*, 983.
(2) For reviews on asymmetric catalysts based upon amino alcohols and molybdenum, vanadium, titanium, aluminum, and boron see: (a) *Catalytic Asymmetric Synthesis*, Ojima, I., Ed.; VCH: Weinheim, 1993. (b) Deloux, L.; Srebnick, M. *Chem. Rev.* **1993**, *93*, 763. (c) Soai, K.; Niwa, S. *Chem. Rev.* **1992**, *92*, 833. (d) Blaser, H. U. *Chem. Rev.* **1992**, *92*, 935. (e) Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 497. (f) Kagan, H. B.; Riant, O. *Chem. Rev.* **1992**, *92*, 1007. (g) Kagan, H. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: Orlando, 1985; Vol. 5, p 28.
(3) (a) Aratani, T.; Yoneyoshi, Y.; Nagase, T. *Tetrahedron Lett.* **1982**, 685. (b) Pfaltz, A. *Chimia* **1990**, *44*, 202. (c) Aratani, T. *Pure Appl. Chem.* **1985**, *57*, 1839. (d) Hayashi, M.; Miyamoto, Y.; Inoue, T.; Oguni, N. *J. Chem. Soc., Chem. Commun.* **1991**, 1752.

(4) (a) Yamada, S.; Mashiko, T.; Terashima, S. *J. Am. Chem. Soc.* **1977**, *99*, 1988. (b) Coleman Kammula, S.; Duim-Koolstra, E. T. *J. Organomet. Chem.* **1983**, *246*, 53. (c) Kagan, H. B.; Mimoun, H.; Mark, C.; Schurig, V. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 485.
(5) (a) Garner, C. D.; Durant, R.; Mabbs, F. E. *Inorg. Chim. Acta* **1977**, *24*, L29. (b) Ueyama, N.; Yano, M.; Miyashita, H.; Nakamura, A.; Kamachi, M.; Nozakura, S. *J. Chem. Soc., Dalton Trans.* **1984**, 1447. (c) Ueyama, N.; Kamabuchi, K.; Nakamura, A. *J. Chem. Soc., Dalton Trans.* **1985**, 635. (d) Miller, K. F.; Wentworth, R. A. D. *Inorg. Chem.* **1977**, *16*, 3385. (e) Tanaka, K.; Honjo, M.; Tanaka, T. *Inorg. Chem.* **1985**, *24*, 2662. (f) Arzoumanian, H.; Corao, C.; Krentzien, H.; Lopez, R.; Teruel, H. *J. Chem. Soc., Chem. Commun.* **1992**, 856. (g) Fusi, A.; Ugo, R.; Zanderighi, G. M. *J. Catal.* **1974**, *34*, 175. (h) Gullotti, M.; Pasini, A.; Zanderighi, G. M.; Ciani, G.; Sironi, A. *J. Chem. Soc. Dalton Trans.* **1981**, 902. (i) Trifirò, F.; Forzatti, P.; Preite, S.; Pasquon, I. *J. Less-Common Met.* **1974**, *36*, 319.
(6) Berti, G.; Bottari, F.; Ferrarini, P. L.; Macchia, B. *J. Org. Chem.* **1965**, *30*, 4091.

from 2D ^{1}H COSY, 2D ^{1}H NOESY, and proton-detected 2D ^{1}H,^{13}C correlations using degassed nonspinning samples. T_1 measurements were obtained by using the inversion recovery method.[7] The following values for selected protons of $N(R)$-2(R)-3(R)-4(S)-(HNO$_2$)MoO$_2$ (**1**) (*vide infra*) were obtained: p-Ph-C$_4$, 1.406(1); m-Ph-C$_4$, 1.333(1); NH, 0.395(5); H$_1\alpha$, 0.366(3) s. 2D NMR spectra were recorded using pulse sequences suitable for phase-sensitive representations using TPPI. The double-quantum filtered ^{1}H COSY experiments[8] were recorded with 1024 increments of size 2K (with 16 scans each) covering the full range (ca. 5000 Hz) in both dimensions. The ^{1}H NOESY measurements[9] were recorded with 1024 increments of size 2K (with 16 scans each) covering the full range (ca. 5000 Hz) in both dimensions and using a mixing time of 0.8 s. The ^{1}H,^{13}C correlation[10] was recorded using the standard HMQC sequence with no decoupling during acquisition, and 1024 increments of size 2K (with 32 scans each) were collected covering the full range in both dimensions (ca. 5000 Hz in F_2 and ca. 21 000 Hz in F_1). ^{31}P NMR spectra were recorded on a Varian VXR 300 spectrometer operating at 121.42 MHz. Chemical shifts are relative to external 85% H$_3$PO$_4$ with downfield values reported as positive. Gas chromatographic analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm FT) SPB-2380 Supelco fused silica capillary column and coupled with a C-R6A Chromatopac operating in the corrected area method. Conductivities were measured with a Model 990101 Orion conductance cell connected to a Model 101 conductivity meter. The conductivity data were obtained at a sample concentration of ca. 10^{-3} M in DMSO solutions at room temperature. Molecular weight measurements of the Mo(VI) complexes were carried out with a Wescan 233 instrument by the differential vapor-pressure method in DMSO at 100 °C (standard: sucrose octaacetate).

Synthesis of the Ligands. [HOCH$_2$-(R)-PhCH]NH[(S)-PhCH-(R)-PhCHOH] [2(R)-3(R)-4(S)-HNO$_2$H$_2$]. A mixture of (R)-(−)-phenylglycinol (3.89 g, 28.4 mmol) and *trans*-stilbene oxide (5.50 g, 28.0 mmol) was heated at 100 °C for 2 days with stirring. On cooling the solution down to room temperature, an orange oil was obtained. This was dissolved in diethyl ether (10 mL) to give a pale yellow solution, from which white crystals separated out on standing at room temperature. The solid was collected by filtration, washed with diethyl ether (2 × 5 mL), petroleum ether (2 × 10 mL), and dried in vacuo to give 2.95 g of diastereomerically pure 2(R)-3(R)-4(S)-HNO$_2$H$_2$ (32% based on phenylglycinol). [α]$^{25}_D$ = −57.2 (c = 10, CHCl$_3$). Anal. Calcd for C$_{22}$H$_{23}$NO$_2$: C, 79.25; H, 6.95; N, 4.20. Found: C, 79.34; H, 6.87; N, 4.22.

[HOCH$_2$-(R)-PhCH]NCH$_3$[(S)-PhCH-(R)-PhCHOH] [2(R)-3(R)-4(S)-MeNO$_2$H$_2$]. A mixture of 2(R)-3(R)-4(S)-HNO$_2$H$_2$ (2.92 g, 8.77 mmol), formaldehyde (3 mL), and formic acid (3 mL) was stirred at 100 °C overnight. After the solution was cooled to 0 °C, the pH value was brought to ca 7.5 by addition of 10% aqueous NaOH. The resulting suspension was extracted with CH$_2$Cl$_2$ (2 × 30 mL). The organic phase was dried over anhydrous Na$_2$SO$_4$ and the solvent removed in vacuo to yield 2(R)-3(R)-4(S)-MeNO$_2$H$_2$ as an off-white solid in 76% yield. [α]$^{25}_D$ = −58.6 (c = 13, CHCl$_3$). Anal. Calcd for C$_{23}$H$_{25}$NO$_2$: C, 79.51; H, 7.25; N, 4.03. Found: C, 79.77; H, 7.31; N, 4.06.

Synthesis of the Complexes. $N(R)$-2(R)-3(R)-4(S)-(HNO$_2$)MoO$_2$ (1). MoO$_2$(acac)$_2$ (0.33 g, 1.00 mmol) was dissolved in warm methanol (∼60 °C, 25 mL). After the solution was cooled to room temperature, 2(R)-3(R)-4(S)-HNO$_2$H$_2$ (0.33 g, 1.00 mmol) in methanol (25 mL) was added causing an immediate color change from yellow-orange to colorless. Slow evaporation of the solvent under a stream of nitrogen gave **1** as off-white crystals in 76% yield. [α]$^{25}_D$ = −24.3 (c = 4, DMSO). Anal. Calcd for C$_{22}$H$_{21}$NMoO$_4$: C, 57.52; H, 4.61; N, 3.05. Found: C, 57.55; H, 4.54; N, 3.11. IR (cm^{-1}: 3208 ν(N−H), 896 ν(Mo=O), 794 ν(Mo=O → Mo).

$N(R)$-2(R)-3(R)-4(S)-(MeNO$_2$)MoO$_2$ (2). MoO$_2$(acac)$_2$ (0.16 g, 0.50 mmol) was dissolved in warm methanol (∼60 °C, 25 mL). After the solution was cooled to room temperature, 2(R)-3(R)-4(S)-MeNO$_2$H$_2$

Table 1. Crystal Data for $N(R)$-2(R)-3(R)-4(S)-(HNO$_2$)MoO$_2$ (**1**)

formula	C$_{22}$H$_{21}$NMoO$_4$
molecular weight	459.34
temperature (K)	293(2)
space group	$P2_12_12_1$ (No. 19)
a (Å)	7.620(3)
b (Å)	13.589(2)
c (Å)	20.339(3)
V (Å^3)	2106.1(9)
Z	4
D_{calc} (g cm^3)	1.449
μ (Mo Kα) (cm^{-1})	6.49
radiation	graphite-monochromated Mo Kα
	λ = 0.71069 Å
no. unique data with $I > 3\sigma(I)$	2125
$R_{2(R)\text{-}N(R)\text{-}4(S)\text{-}3(R)}{}^a$	0.0336
$R_{w\ 2(R)\text{-}N(R)\text{-}4(S)\text{-}3(R)}{}^b$	0.0843
$R_{2(S)\text{-}N(S)\text{-}4(R)\text{-}3(S)}/R_{2(R)\text{-}N(R)\text{-}4(S)\text{-}3(R)}$	0.03(8)

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

(0.17 g, 0.50 mmol) in methanol (25 mL) was added. Slow diffusion of diethyl ether vapors into the resulting colorless solution gave off-white crystals of **2** in 70% yield. [α]$^{25}_D$ = +101.3 (c = 2, DMSO). Anal. Calcd for C$_{23}$H$_{23}$NMoO$_4$: C, 58.36; H, 4.90; N, 2.96. Found: C, 58.58; H, 4.82; N, 3.01. IR (cm^{-1}: 948, 902 ν(Mo=O).

Reaction of $N(R)$-2(R)-3(R)-4(S)-(MeNO$_2$)MoO$_2$ (2) with PPh$_3$. **(a)** In a sealed NMR tube, a mixture of **2** (0.02 g, 0.04 mmol) and PPh$_3$ (0.01 g, 0.04 mmol) in degassed, dry DMF-d_7 (0.7 mL) was heated at 100 °C for 4 days. The color of the solution slowly turned dark green. After cooling to room temperature, analysis by ^{31}P NMR spectroscopy showed that PPh$_3$ had completely converted to OPPh$_3$ (δ 26.2 ppm). No trace of paramagnetic compounds was found in the solution (Evans method), which was analyzed by ^{1}H NMR spectroscopy. The formation of a Mo(IV) species can be proposed on the basis of the NMR study which showed all the proton resonances to shift upfield as compared to the Mo(VI) precursor. ^{1}H NMR (DMF-d_7, 294 K): 5.51 (d, H$_3$, J_{34} = 6.2 Hz); 4.72 (dd, H$_{1\alpha}$, $J_{1\alpha1\beta}$ = 8.7 Hz, $J_{1\alpha2}$ = 2.7 Hz); 4.50 (t, H$_2$, $J_{1\beta2}$ = 2.3 Hz); 4.26 (dd, H$_{1\beta}$); 4.35 (d, H$_4$); 2.57 (s, CH$_3$). Furthermore, the starting Mo(VI) complex **2** was regenerated by simply adding a few drops of DMSO to the dark green solution of the Mo(IV) species. GC analysis showed the stoichiometric conversion of DMSO to dimethyl sulfide.

(b) In a sealed NMR tube, a 1:10 mixture of **2** (0.02 g, 0.04 mmol) and PPh$_3$ (0.10 g, 0.40 mmol) in degassed, dry DMSO-d_6 (0.7 mL) was heated at 100 °C for 4 days. The color of the solution remained unchanged. After the solution was cooled to room temperature, analysis by ^{31}P NMR spectroscopy showed that PPh$_3$ had completely converted to OPPh$_3$, while the ^{1}H NMR spectrum was identical with that of an authentic sample of **2** in DMSO-d_6. The presence of dimethyl sulfide in the reaction mixture was detected by gas chromatographic analysis.

X-ray Data Collection and Processing. Crystal and intensity data for $N(R)$-2(R)-3(R)-4(S)-(HNO$_2$)MoO$_2$ (**1**) are reported in Table 1. X-ray measurements were performed on an Enraf-Nonius CAD4 diffractometer. The cell constants and orientation matrix were determined by least-squares refinement of the setting angles for 25 reflections. The intensities of three standard reflections were measured every 120 min of X-ray exposure (Mo Kα). No decay was observed. The data were corrected for Lorentz and polarization effects. An empirical correction for the absorption effect was made by using the program DIFABS.[11]

Solution and Refinement of the Structure. All the calculations were carried out on a Digital DEC 5000/200 computer by using the SHELX93[12] and ORTEP[13] programs. Atomic scattering factors for non-hydrogen atoms were taken from ref 14 and for hydrogen atoms from

(7) Vold, R. L.; Waugh, J. S.; Klein, M. P.; Phelps, D. E. *J. Chem. Phys.* **1968**, *48*, 3831.

(8) Shaka, A. J.; Freeman, R. *J. Magn. Reson.* **1983**, *51*, 169.

(9) Sklener, V.; Miyashiro, H.; Zon, G.; Miles, H. T.; Bax, A. *FEBS Lett.* **1986**, *208*, 94.

(10) Summers, M. F.; Marzilli, L. G.; Bax, A. *J. Am. Chem. Soc.* **1986**, *108*, 4285.

(11) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(12) Sheldrick, G. M. *J. Appl. Chem.* Manuscript in preparation.

(13) Johnson, C. K. ORTEP. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

(14) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, p 99.

(15) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(16) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* Manuscript in preparation.

Table 2. Atomic Parameters for the structure of
$N(R)$-$2(R)$-$3(R)$-$4(S)$-(Hno$_2$)MoO$_2$ (**1**)

atom	x	y	z	U(eq)
Mo	2059(1)	7562(1)	9903(1)	25(1)
O1	2792(6)	8379(3)	9325(2)	38(1)
O2	−163(4)	7433(3)	9728(2)	33(1)
O3	2843(6)	6331(3)	9575(2)	29(1)
O4	1807(6)	8397(3)	10643(2)	34(1)
N	1911(8)	6483(3)	10792(2)	28(1)
C1	1311(9)	8056(4)	11278(3)	37(1)
C2	2196(8)	7058(4)	11404(2)	31(1)
C3	3104(7)	5435(4)	9928(3)	29(1)
C4	3209(8)	5693(4)	10671(2)	29(1)
C(1,2)	1593(5)	6563(3)	12029(2)	37(1)
C(2,2)	−168(5)	6348(2)	12136(2)	51(2)
C(3,2)	−677(5)	5851(4)	12702(2)	68(2)
C(4,2)	575(6)	5568(4)	13161(2)	65(2)
C(5,2)	2336(6)	5783(4)	13055(2)	67(2)
C(6,2)	2845(4)	6280(3)	12489(2)	56(2)
C(1,3)	1700(5)	4692(3)	9742(2)	34(1)
C(2,3)	−7(5)	4983(2)	9598(2)	44(2)
C(3,3)	−1256(4)	4284(3)	9425(2)	60(2)
C(4,3)	−800(6)	3294(3)	9397(2)	66(2)
C(5,3)	906(7)	3004(2)	9541(3)	70(2)
C(6,3)	2156(5)	3703(3)	9714(2)	50(2)
C(1,4)	3177(6)	4814(3)	11135(2)	39(1)
C(2,4)	1629(5)	4349(4)	11320(2)	50(2)
C(3,4)	1670(6)	3586(4)	11776(3)	69(2)
C(4,4)	3260(8)	3288(3)	12046(2)	85(3)
C(5,4)	4808(6)	3753(4)	11860(3)	86(3)
C(6,4)	4766(5)	4516(4)	11405(3)	59(2)

^{a} Thermal parameters multiplied by 1000, coordinates by 10 000. U(eq) defined as one-third of the trace of the orthogonalized thermal tensor.

ref 15. Anomalous dispersion terms, both real and imaginary, were included for non-hydrogen atoms. The structure was solved by direct methods using the SIR92 program,[16] and all of the non-hydrogen atoms were found through a series of F_o Fourier maps. Hydrogen atoms were introduced at calculated positions. Phenyl rings were treated as rigid bodies. Refinement was done by full-matrix least-squares calculations, initially with isotropic thermal parameters. In the last least-squares cycles anisotropic thermal parameters were used for the Mo, N, and O atoms, and the chain carbon atoms. The refinement converged to $R = 0.0336$ and $R_w = 0.0843$ factors. The ΔF final maps appeared essentially featureless. Final positional parameters of non-hydrogen atoms are reported in Table 2. The value $R = R_{w\ 2(S)-N(S)-4(R)-3(S)}/R_{w\ 2(R)-N(R)-4(S)-3(R)}$ of 0.03(8) confirms the correct assignment of the absolute configuration of each stereocenter.

Results and Discussion

Synthesis of the Ligands. The nucleophilic attack by primary or secondary amines on epoxides is a common procedure for the preparation of β-amino diols.[17] This synthetic protocol has been used in this work to synthesize the chiral N,O$_2$ mixed-donor ligand $2(R)$-$3(R)$-$4(S)$-HNO$_2$H$_2$ by reaction of enantiomerically pure (R)-phenylglycinol with *rac-trans*-stilbene oxide at 100 °C for 2 days (Scheme 1). In actuality, the stereochemistry of the *trans*-stilbene oxide ring-opening reaction imposes the formation of two diastereomers, $2(R)$-$3(R)$-$4(S)$-HNO$_2$H$_2$ and $2(R)$-$3(S)$-$4(R)$-HNO$_2$H$_2$ (see Figure 3 for the labeling scheme), and in fact, ^{1}H and ^{13}C NMR spectroscopy shows the crude reaction mixture to contain two diastereomeric products in a ca. 1:1 ratio (Tables 3 and 4).[18] However, one

diastereomer, namely, $2(R)$-$3(R)$-$4(S)$-HNO$_2$H$_2$, can be isolated in 32% yield by crystallization of the crude reaction product from diethyl ether, followed by several washings with petroleum ether.

The *N*-methyl substituted derivative $2(R)$-$3(R)$-$4(S)$-MeNO$_2$H$_2$ was obtained with retention of configuration of all asymmetric carbon centers by treatment of the secondary amine precursor with HCOOH/H$_2$CO.

To determine by NMR spectroscopy the relative configurations of the unique diastereomeric isolated HNO$_2$H$_2$ ligand and of its methylated derivative, metal complexes of these ligands were synthesized. In this way, in fact, one can obtain a ligand framework which is sufficiently rigid to allow the determination of its preferred time-averaged conformation and tridimensional structure by ^{1}H NOESY spectroscopy.

Synthesis of the Molybdenum Complexes. The ligand-exchange reactions of MoO$_2$(acac)$_2$ with $2(R)$-$3(R)$-$4(S)$-HNO$_2$H$_2$ and $2(R)$-$3(R)$-$4(S)$-MeNO$_2$H$_2$ in methanol give the molybdenyl complexes $N(R)$-$2(R)$-$3(R)$-$4(S)$-(HNO$_2$)MoO$_2$ (**1**) and $N(R)$-$2(R)$-$3(R)$-$4(S)$-(MeNO$_2$)MoO$_2$ (**2**), respectively, in pure diastereomeric form as shown by ^{1}H NMR spectroscopy (Scheme 1). Both complexes are readily soluble in DMSO and DMF in which they behave as nonelectrolytes, whereas they poorly dissolve in any other solvent (*e.g.*, MeNO$_2$, MeOH, CH$_2$Cl$_2$, or CDCl$_3$).

Solid-State Structure of 1. An X-ray diffraction analysis has been carried out on **1**. The structure consists of a "linear" polymeric chain of $N(R)$-$2(R)$-$3(R)$-$4(S)$-(HNO$_2$)MoO$_2$ molecules connected through unsymmetrical Mo=O → Mo bridges. ORTEP views of the mononuclear unit and of a section of the polymeric material are reported in Figures 1 and 2, respectively, while selected bond distances and angles are reported in Table 5.

Each metal center is coordinated in a distorted octahedral geometry by a *cis* dioxo unit (O1 and O2) and by two *trans* alkoxo atoms (O3 and O4). The coordination polyhedron is completed by a nitrogen atom (*trans* to O1) and by a bridging O2$_b$ atom from an adjacent molecule (*trans* to O2). The Mo−O distances in the repeating O → Mo=O bridging unit are markedly different [Mo−O2 = 1.739(4) Å, Mo−O2$_b$ = 2.246(4) Å]. In particular, the separation between each Mo center and the oxo oxygen atom (O2$_b$) from the neighboring complex molecule is longer than the sum of the covalent radii (2.03 Å) and thus is consistent with a weak bonding interaction. The Mo−O distances in the dioxo MoO$_2$ moiety [1.739(4) and 1.711(4) Å], the two Mo−O alkoxo distances [1.897(4) and 1.895(4) Å], and the Mo−N distance [2.331(4) Å] fall in the proper range for analogous complexes with the MoO$_2^{2+}$ core.[19,20] The most evident distortions from the idealized octahedral geometry are shown by the N−Mo−O3 [74.5(2)°], N−Mo−O4 [75.9(2)°], and O3−Mo−O4 [147.1(2)°] angles, likely as a consequence of the strain of the five-membered chelate ring. As a result, the two alkoxo atoms are bent toward the nitrogen atom. The aliphatic carbon atoms lie below the N−Mo−O3−O4 *pseudo*plane, with the exception of the C1 atom which is almost coplanar. The Ph−C3 ring lies above this plane and adopts a *pseudo*axial position [Mo−O3−C3−C3,1 = 109.0(2)°], while the other phenyls occupy a *pseudo*equatorial position.

(17) (a) Houben-Weyl, G. *Methoden der Organischen Chemie*; Thieme Verlag: Stuttgart, 1957; Band XI/1, p 311. (b) Curtin, D. Y.; Kellom, D. B. *J. Am. Chem. Soc.* **1953**, *75*, 6011.

(18) NMR data for the $2(R)$-$3(R)$-$4(S)$ diastereomer are reported in Table 3 and Table 4. ^{1}H NMR (CDCl$_3$) data for the $2(R)$-$3(S)$-$4(R)$ diastereomer, not isolated in the solid state, have been obtained from the crude reaction mixture: δ 4.71 (d, H$_3$, J_{34} = 5.7 Hz), 4.06 (d, H$_4$), 3.52 (m, H$_{1\beta}$), other proton resonances are masked by those of the $2(R)$-$3(R)$-$4(S)$ diastereomer.
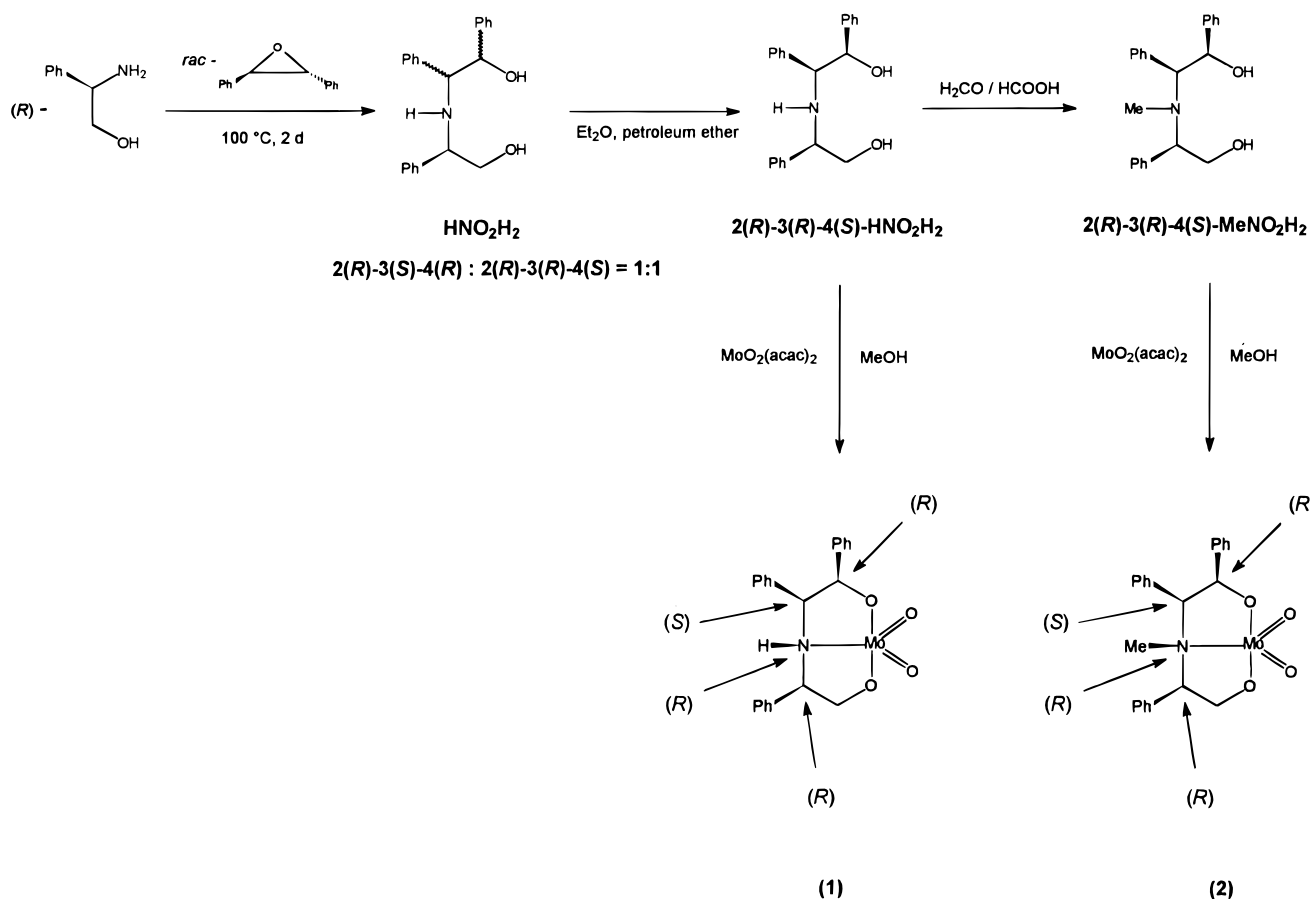
(19) Barbaro, P.; Bianchini, C.; Scapacci, G.; Masi, D.; Zanello, P. *Inorg. Chem.* **1994**, *33*, 3180.

(20) (a) Stiefel, E. I. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 3, p 1375. (b) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.

(21) Bhattacharjee, S.; Bhattacharyya, R. *J. Chem. Soc., Dalton Trans.* **1993**, 1151.

(22) Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1983**, *22*, 1768.

Scheme 1

$2(R)$-$3(S)$-$4(R)$: $2(R)$-$3(R)$-$4(S)$ = 1:1

Table 3. Selected ^{1}H NMR Spectral Data^a

proton	2(R)-3(R)-4(S)-HNO$_2$H$_2$^{b}	2(R)-3(R)-4(S)-MeNO$_2$H$_2$^{b}	N(R)-3(R)-4(S)-(HNO$_2$)MoO$_2$ (1)^c	N(R)-2(R)-3(R)-4(S)-(MeNO$_2$)MoO$_2$ (2)^c
	chemical shift (ppm)			
H$_1$$^\alpha$	3.76^{e,g}	3.86 (dd)^g	4.85 (t)	5.41 (t)
H$_1$$^\beta$	3.61^{e,g}	3.65 (dd)^g	4.66 (dd)	4.67 (dd)
H$_2$	3.75^e	4.06 (dd)	4.45 (td)	4.99 (dd)
H$_3$	4.99 (d)	5.47 (d)	5.91 (d)	6.28 (d)
H$_4$	3.94 (d)	4.02 (d)	4.97 (dd)	4.93 (d)
OH	1.9 (2H, bs)	2.2 (2H, bs)		
NH	2.9 (bs)		5.82 (t)	
NCH$_3$		2.20 (s)		2.70 (s)
o-Ph-C$_2$	f	f	7.34	7.44
o-Ph-C$_3$	f	f	7.19	7.17
o-Ph-C$_4$	f	f	6.72	6.96

couple	2(R)-3(R)-4(S)-HNO$_2$H$_2$	2(R)-3(R)-4(S)-MeNO$_2$H$_2$	N(R)-3(R)-4(S)-(HNO$_2$)MoO$_2$ (1)	N(R)-2(R)-3(R)-4(S)-MeNO$_2$H$_2$ (2)
	coupling constant J (Hz)			
H$_1$$^\alpha$,H$_1$$^\beta$	11.4^e	11.0	10.8	11.2
H$_1$$^\alpha$,H$_2$	−7.6^{e,g}	8.9^g	10.8	11.2
H$_1$$^\beta$,H$_2$	4.7^{e,g}	5.0^g	4.9	5.4
H$_3$,H$_4$	5.5	7.2	7.0	6.2
NH,H$_2$			10.8	
NH,H$_4$			10.8	

^{a} 500.132 MHz, 298 K. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qi, quintet; b, broad. Unresolved multiplet unless otherwise specified. See Figure 3 for the labeling scheme. ^{b} In CDCl$_3$. ^{c} In DMSO-d_6. ^{e} Second order ABC spin system: data from computer simulation.^{f} Not assigned. ^{g} α and β labels may be exchanged.

Each monomeric unit contains four stereocenters, namely the C2, C3, and C4 carbon atoms and the coordinated nitrogen atom, with the absolute configurations $N(R)$-$2(R)$-$3(R)$-$4(S)$, respectively.

Polymerization of LMo^{VI}O$_2$ complexes (L = tridentate ligand) in the solid state through Mo=O → Mo bridges is quite common,[21−23] whereas only two monomeric five-coordinate species are known.[19,24] In particular, the Mo=O$_b$ → Mo lengths in **1** are comparable with those found by Berg and Holm in [MoO$_2$(L−NO$_2$)]$_n$ (L−NO$_2$ = pyridine-2,6-dimethanolate).[22] In this compound the adjacent monomeric molecules are twisted along the polymeric chain, a feature also observed in **1** and shown by the N−Mo−Mo′−N′ [179.8(2)°] and O1−Mo−Mo′−O1′ [178.4(2)°] torsion angles.

(23) Rajan, O. A.; Chakravorty, A. *Inorg. Chem.* **1981**, *20*, 660.

(24) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 917.

Table 4. Selected ^{13}C NMR Spectral Data[a]

	chemical shifts (ppm) and coupling constants ($^1J_{HC}$ (Hz))			
carbon	2(R)-3(R)-4(S)-HNO$_2$H$_2$[b]	2(R)-3(R)-4(S)-MeNO$_2$H$_2$[b]	N(R)-2(R)-3(R)-4(S)-(HNO$_2$)MoO$_2$ (**1**)[c]	N(R)-2(R)-3(R)-4(S)-(MeNO$_2$)MoO$_2$ (**2**)[c]
C$_1$	75.87 (145.8)	62.00 (144.6)	80.68 (143.5)	76.5 (145.0)
C$_2$	71.40 (133.6)	67.25 (135.0)	69.55 (142.0)	71.0 (140.9)
C$_3$	86.21 (143.7)	73.75 (141.8)	91.60 (145.8)	88.4 (143.7)
C$_4$	76.18 (142.4)	74.50 (137.5)	71.26 (139.8)	75.8 (136.9)
NCH$_3$		33.31 (134.7)		37.8 (137.5)
o-Ph-C$_2$	d	d	127.92 (157.8)	130.85 (158.0)
o-Ph-C$_3$	d	d	126.87 (158.6)	126.85 (156.3)
o-Ph-C$_4$	d	d	127.81 (159.7)	131.49 (159.6)

[a] 125.77 MHz, 298 K. See Figure 3 for the labeling scheme. [b] In CDCl$_3$. [c] In DMSO-d_6. [d] Not assigned.
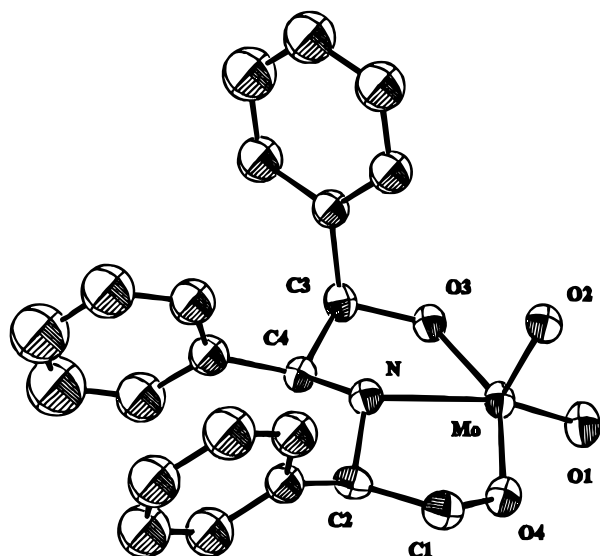
Figure 1. ORTEP drawing of the monomeric unit of the complex N(R)-2(R)-3(R)-4(S)-(HNO2)MoO$_2$ (**1**). Hydrogen atoms are not shown for clarity.
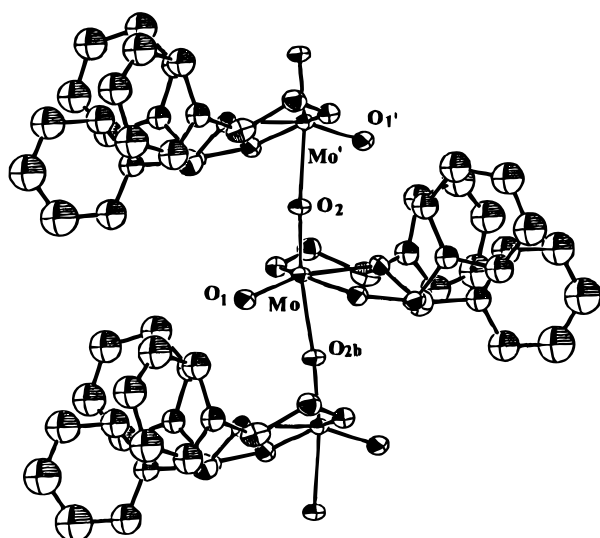
Figure 2. ORTEP drawing showing the polymeric structure of the complex N(R)-2(R)-3(R)-4(S)-(HNO$_2$)MoO$_2$ (**1**). Hydrogen atoms are not shown for clarity.

Magnetic Resonance Spectra and Solution Structure. Selected ^{1}H and ^{13}C NMR data for **1** and **2** in DMSO-d_6 solutions are collected in Tables 3 and 4, respectively. The assignments of the signals have been made on the basis of 2D ^{1}H COSY, 2D ^{1}H NOESY, and proton-observed 2D ^{1}H,^{13}C correlations.

Upon coordination to molybdenum, the stereochemistry of the amino diol ligands in **1** and **2** is evidently complicated by the creation of a fourth asymmetric center (the nitrogen atom). However, NMR spectroscopy shows both compounds to be

Table 5. Selected Bond Distances (Å) and Angles (deg) for N(R)-2(R)-3(R)-4(S)-(HNO$_2$)MoO$_2$ (**1**)

Mo−O1	1.711(4)	Mo−O4	1.895(4)
Mo−O2	1.739(4)	Mo-N	2.331(4)
Mo−O3	1.897(4)	Mo−O2$_b$	2.246(4)
O1−Mo−O2	104.0(2)	O2$_b$−Mo−O4	80.1(2)
O1−Mo−O3	103.2(2)	O1−Mo−O2$_b$	85.4(2)
O1−Mo−N	163.2(2)	O3−Mo−O4	147.1(2)
O1−Mo−O4	100.9(2)	O2−Mo−N	92.8(2)
O2$_b$−Mo−O2	170.54(5)	O1−Mo−N−C2	66.2(4)
O2$_b$−Mo−O3	79.8(2)	O1−Mo−N−C4	58.2(4)
O2$_b$−Mo−N	77.8(2)		

diastereomerically pure, thus indicating the stereoselective coordination of the nitrogen also in solution.

A section of the ^{1}H NOESY spectrum of **1** is reported in Figure 3. The couple of diastereotopic protons H$_{1\alpha}$ (conventionally, the one above the N−Mo−O$_3$−O$_4$ *pseudo*plane, see Figure 3) and H$_{1\beta}$ (below) can unequivocally be assigned by the NOEs from H$_{1\alpha}$ to the *ortho*-Ph−C$_2$ and from H$_{1\beta}$ to H$_2$, respectively. The aromatic proton resonances can be divided into separate sets corresponding to each phenyl ring by means of 2D ^{1}H COSY and ^{1}H,^{13}C correlations. The *ortho*-phenyl protons of each ring are then identified by the strong NOEs with the aliphatic proton in the β position (*i.e.*, the *ortho*-Ph-C$_2$ has NOE with H$_2$, and so on). The most significant NOEs are (i) those of the NH proton with the *ortho* protons of *each* phenyl ring, (ii) that of H$_2$ with H$_4$ (not shown in Figure 3), and (iii) that from H$_{1\alpha}$ to NH (not shown in Figure 3). Thus, assuming the (R) configuration at the C$_2$ stereocenter of the starting phenylglycinol, these cross-peaks indicate that the NH proton as well as the Ph-C$_4$ and Ph-C$_3$ rings lie above the O−N−O−Mo *pseudo*plane. This means that the absolute configuration of the asymmetric centers of **1** is N(R)-2(R)-3(R)-4(S) which, in fact, has been shown by the X-ray diffraction analysis. With the exception of the NOE between the Ph-C$_3$ and Ph-C$_4$ *ortho* protons, no further interaromatic ring cross-peaks are shown in the NOESY spectrum of **1**. This suggests the existence of a stacking interaction between the phenyl rings, and indeed, the X-ray crystal structure shows the three phenyl rings to be almost parallel to each other in the solid state.

A section of the ^{1}H NOESY spectrum of **2** is reported in Figure 4. The assignment of the signals was carried out as described above for **1**. The *ortho*-Ph-C$_3$ protons in **2** are partially overlapped with other aromatic protons but, nevertheless, can be located at 7.17 ppm by the ^{1}H COSY and ^{1}H,^{13}C correlation. Again, the crucial NOEs are those between (i) the CH$_3$ protons and the *ortho* protons of *each* phenyl ring, (ii) H$_2$ and H$_4$, (iii) H$_2$ and H$_3$, and (iv) H$_{1\alpha}$ and the CH$_3$ group. Thus, given the (R) configuration at the C$_2$ stereocenter of the starting phenylglycinol, these cross-peaks indicate that the methyl protons as well as the Ph-C$_4$ and Ph-C$_3$ rings lie above the O−N−O−Mo *pseudo*plane, consistent with the absolute configuration N(R)-2(R)-3(R)-4(S) of the asymmetric centers.
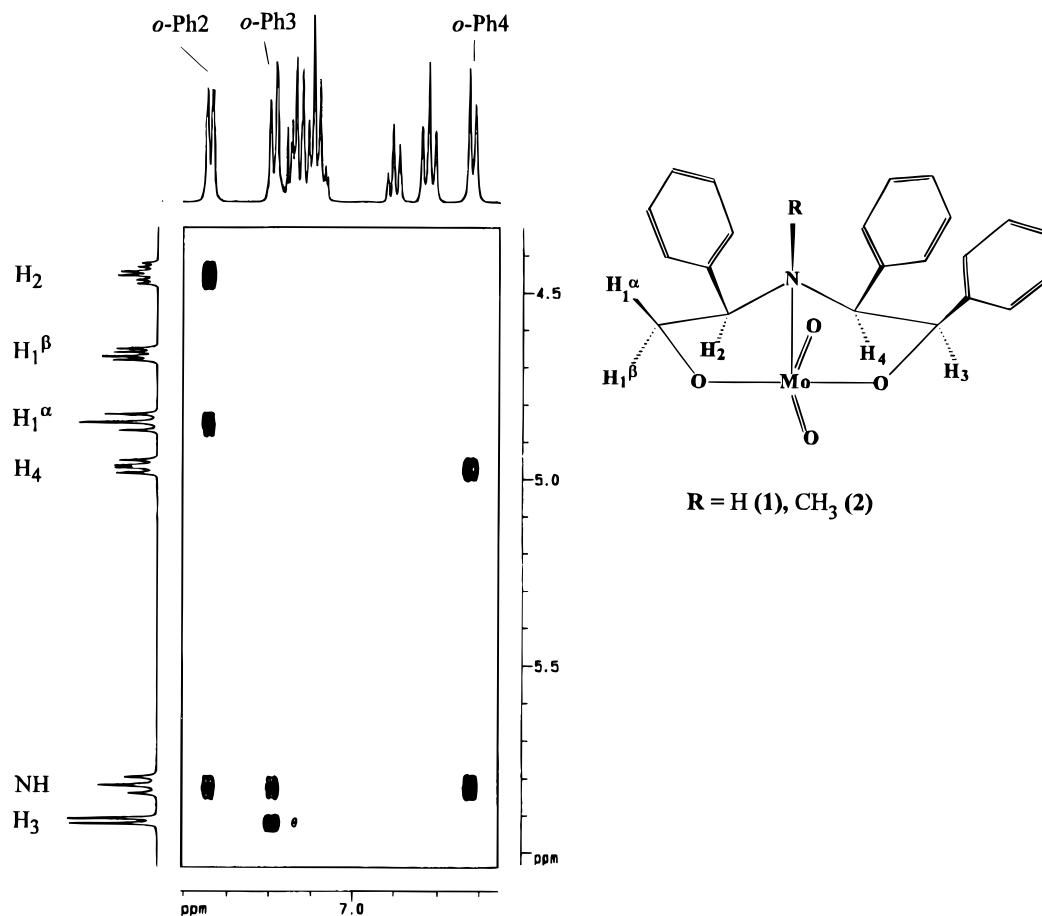
Figure 3. Section of the 2D ^{1}H NOESY spectrum of **1** (500.132 MHz, DMSO-d_6, 298 K) and sketch of the labeling scheme adopted. All cross-peaks are negative phased.

In conclusion, NMR spectroscopy shows that **1** maintains in solution the primary geometry found in the solid state. It remains to clarify whether the compound is still polymeric in solution or exists as single molecules, eventually stabilized by the solvent. Indeed, the cleavage of the Mo=O → OMo bridges in related MoO$_2$(L) oligomers readily occurs in coordinating solvents (L = NO$_2$ donor-atom ligands).[22,24] In the case at hand, the structural changes of the complexed ligands in either distorted octahedral or trigonal-bipyramidal geometry should be so small that the existence of five-coordinate monomers in solution cannot be proven by ^{1}H NOESY measurements. However, the NOESY spectra of **1** and **2** in DMSO-d_6 do not show any NOEs cross-peaks relating the solvent resonances to those of other protons of the complexes. Also, both the elemental analyses and the ^{1}H NMR spectra in MeOH-d_4 of **1** and **2** recrystallized from DMSO/n-BuOH/n-heptane show that the samples do not contain DMSO. In conclusion, although we were not able to perform reliable molecular weight measurements with the differential vapor-pressure method due to the actual solubility of the complexes only in DMSO and DMF (for **1** a value of 620 ± 30 was found for a calculated value of 459), we do think that the weak bonding interaction responsible for the polymerization of the complexes in the solid state is most likely cancelled in solution by solvation without effective coordination of either DMSO or DMF.

In deoxygenated DMSO or DMF solutions, **2** reacts, though slowly and at high temperature, with triphenylphosphine to give OPPh$_3$. The complex oxidizes completely 1 equiv of PPh$_3$ to

OPPh$_3$ in ca. 4 days at 100 °C in DMF solution, whereas the reaction is catalytic in DMSO where a 10-fold excess of substrate is consumed in ca. 4 days at 100 °C. At the end of the catalytic reaction in DMSO, a colorless solution is obtained from which all the starting molybdenum complex can be recovered intact.

The first step of the proposed catalytic reaction involves the transfer of an oxygen atom to PPh$_3$ from the Mo(VI)O$_2$ unit, which is converted to a transient Mo(IV)O complex. This latter species regenerates the catalyst by oxygen transfer from DMSO which is converted to dimethyl sulfide (GC) (Scheme 2). The intermediacy of a Mo(IV) species is unambiguously shown by *in situ* ^{1}H NMR spectroscopic analysis (see Experimental Section) on the mixture obtained by reacting **2** with a stoichiometric amount of PPh$_3$ in DMF-d_7. Indeed, the reaction in DMF produces a dark green diamagnetic solution, containing a Mo-(IV) species, which, however, could not be isolated due to its extreme sensitivity to moisture. On the other hand, the addition of DMSO to the DMF solution of the oxo Mo(IV) complex regenerates the dioxo Mo(VI) precursor.

Following the transfer of an oxygen atom to a substrate from a dioxo Mo(VI) complex, stable monomeric Mo(IV)O solvent

(25) Craig, J. A.; Harlan, E. W.; Snyder, B. S.; Whitener, M. A.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 2082.

(26) (a) Boyd, I. W.; Spence, J. T. *Inorg. Chem.* **1982**, *21*, 1602. (b) Chen, G. J. J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1976**, *15*, 2612.

(27) Garner, C. D.; Durant, R.; Mabbs, F. E. *Inorg. Chim. Acta* **1977**, *24*, L29.

(28) Pickett, C.; Kumar, S.; Vella, P. A.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 908.

(29) Speier, G. *Inorg. Chim. Acta* **1979**, *32*, 139.

(30) Reynolds, M. S.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1984**, *23*, 3057.

(31) (a) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 925. (b) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401 and references therein. (c) Xiao, Z.; Young, C. G.; Enemark, J. H.; Wedd, A. G. *J. Am. Chem. Soc.* **1992**, *114*, 9194. (d) Schultz, B. E.; Holm, R. H. *Inorg. Chem.* **1993**, *32*, 4244. (e) Schultz, B. E.; Gheller, S. F.; Muetterties, M. C.; Scott, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 2714.
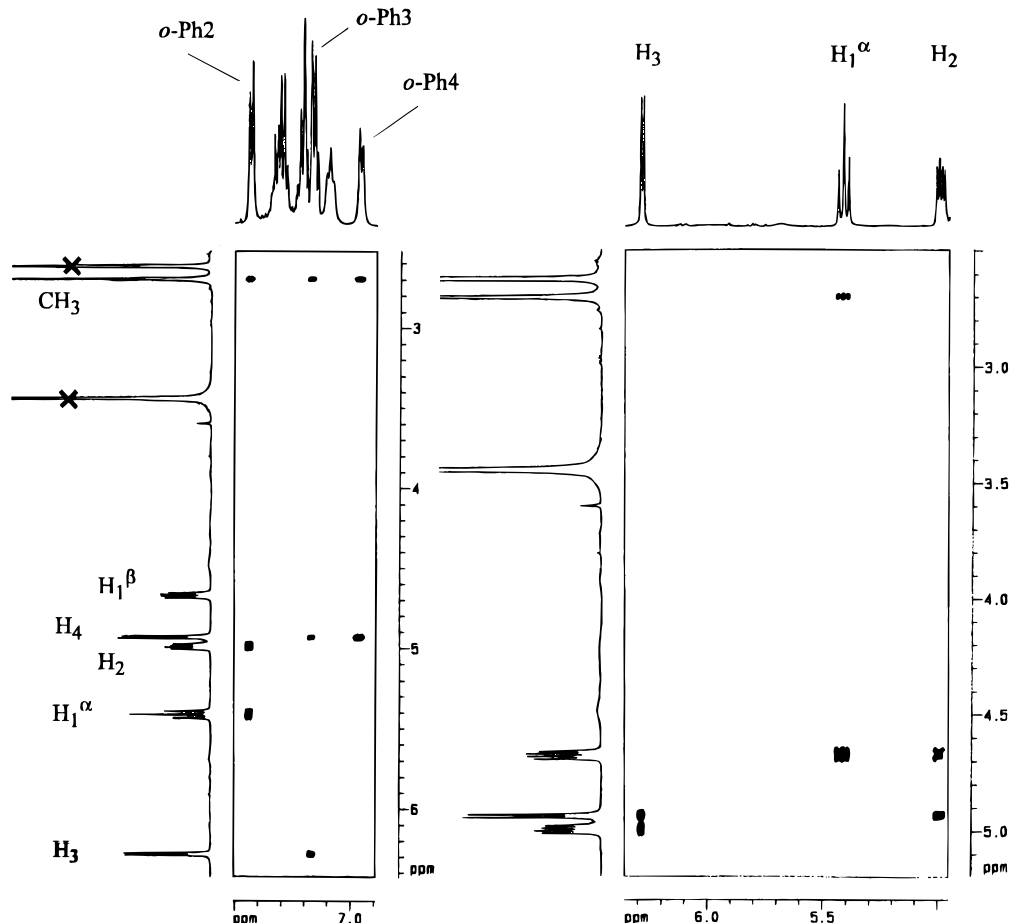
Figure 4. Sections of the 2D ^{1}H NOESY spectrum of **2** (500.132 MHz, DMSO-d_6, 298 K). All cross-peaks are negative phased. Diagonal peaks (positive phased) are not shown on the right section for simplicity. Residual water and solvent proton resonances are marked with an X. For the labeling scheme see Figure 3.

Scheme 2
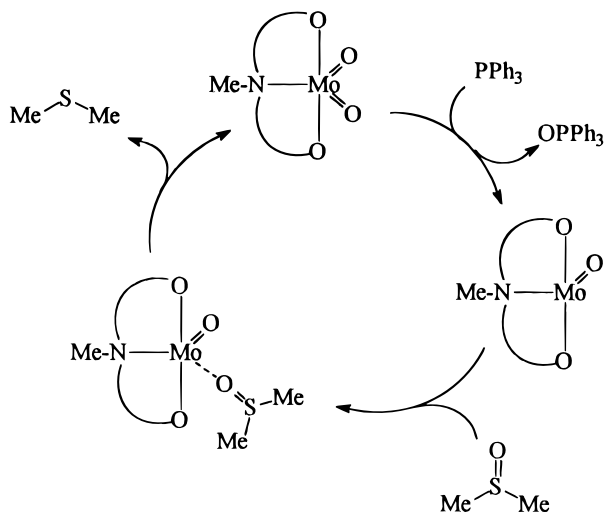
derivatives are generally obtained by using sterically hindered ligands,[21,24-26] while dimerization to give Mo^{V}O—O—Mo^{V}O species occurs when the complexes carry a nonbulky ligand.[19,27-30] In the peculiar case of bulky ligands and DMSO solutions the reactions are commonly

catalytic through a mechanism similar to that illustrated in Scheme 2.[24,31]

Oxygen-transfer reactions to tertiary phosphines have previously been observed for dioxomolybdenum(VI) complexes stabilized by thiolate ligands. To the best of our knowledge, there is only one other example[26a] in which the transfer has been reported to take place from a molybdenyl complex carrying an O—N—O donor set ligand.[19,21,24,32]

Current investigations in our laboratory center on developing the asymmetric reactivity of these new amino diol ligands in conjuction with various electrophilic metal systems as well as the synthesis of the amino dithiol analogues with the scope of increasing the reactivity of the dioxomomlybdenum(VI) complexes in oxygen-transfer reactions.

Supporting Information Available: Tables of the complete set of crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, complete bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters (5 pages). Ordering information is given on any current masthead page.

(32) Roberts, S. A.; Young, C. G.; Cleland, W. E., Jr.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1988**, *27*, 3044.

IC951464E