Structural Studies of Mono- and Dimetallic Mo^{VI} Complexes − A New Mechanistic Contribution in Catalytic Olefin Epoxidation Provided by Oxazoline Ligands

José A. Brito,[a] Montserrat Gómez,*[a] Guillermo Muller,[a] Helena Teruel,*[b] Jean-Claude Clinet,[c] Elisabet Duñach,[c] and Miguel A. Maestro[d]

Keywords: Molybdenum / Chiral oxazolines / Selective epoxidation / Oxo peroxo complexes / Catalysis

New seven-coordinate oxo(peroxo)molybdenum(VI) complexes with bidentate chiral oxazolines, anionic κ^2-*N*,*O* (**V**) and neutral κ^2-*N*,*N* (**VI**), have been prepared and fully characterised by NMR spectroscopy and single-crystal X-ray diffraction studies. Dimetallic dioxo(μ-oxo)molybdenum(VI) compounds containing oxazolinylpyridine ligands **II**–**IV** have also been synthesised. NMR studies showed the presence of several isomers (up to six species) due to the Mo–O–Mo bridge angle and the unsymmetrical nature of the N,N ligand. The roles of mono- (**I**, **V** and **VI**) and dimetallic (**II**) oxomolybdenum(VI) complexes in the catalytic epoxidation of cyclooctene, norbornene and (*R*)-limonene have been studied. The high activity of the oxomono(peroxo) precursor **V** containing the hemilabile oxazolinylphenolate, in contrast to the unexpected low activity for the oxobis(peroxo) species **VI**, could be justified by the inertness observed for the oxazolinylpyridine ligand. In addition, the dimetallic system **II** afforded high selectivity towards limonene epoxide formation (*trans*/*cis*-**10** ratio up to 9:1).

Introduction

High-valent oxometal species have demonstrated the ability to catalyse the oxidation of a variety of organic substrates by homogeneous as well as heterogeneous routes.[1,2] In particular, the Mo-catalysed alkene-to-epoxide conversion has received most attention due to its industrial interest. However, the oxygen transfer mechanism is still a controversial subject and three main hypotheses have dominated the discussion. Mimoun suggested that the olefin coordinates to the metal atom before subsequent insertion into the η^2-Mo−O_2 bond to form a five-membered alkyl peroxide metallacycle.[3,4] Coordination of the olefin to the metal centre makes the olefin electrophilic and thus ready for further reaction with a peroxo group acting as a nucleophile. On the other hand, Sharpless proposed a concerted reaction mechanism involving a direct attack by the olefin on the peroxo oxygen atom (with a three-membered ring intermediate).[5] In this case, the coordinated peroxo group is thought to have a sufficiently increased electrophilic character by decreasing the negative charge on the peroxo oxygen atoms. A "hybrid" mechanism was proposed by Jørgensen and Hoffman in which intramolecular slipping of the olefin after coordination to the metal atom, which depends on their relative orientation, was believed to form a three-membered metallacycle intermediate.[6,7]

In terms of the spectator part of the catalyst molecule, S-, N- and O-donor ligands have been mainly used because of their stability towards oxidation processes. However, under catalytic conditions, they frequently suffer partial decoordination.[8,9] This fact discourages their use as selective catalysts in certain organic processes.

Oxazolines have been used as stabilising agents for many transition metals based on their robustness under a variety of reaction conditions when coordinated.[10] Consequently, they have been frequently employed in asymmetric catalytic organic transformations.[11,12]

We have been carrying out research with dioxomolybdenum(VI) compounds (type-**I** complexes, Figure 1) and we herein describe the first examples of oxo(peroxo) and dioxodimetallic molybdenum complexes containing chiral bidentate oxazoline ligands (Figure 1). Both types of systems have been explored as catalytic precursors in olefin epoxid-

[a] Departament de Química Inorgànica, Universitat de Barcelona, Martí I Franquès 1−11, 08028 Barcelona, Spain
Fax: (internat.) + 34-934907725
E-mail: montserrat.gomez@qi.ub.es
[b] Departamento de Química, Universidad Simón Bolívar, Baruta 89000, Caracas 1081, Venezuela
[c] Laboratoire de Chimie Bioinorganique UMR 6001, Université de Nice-Sophia Antipolis, 06108 Nice Cédex 2, France
[d] Departamento de Química Fundamental, Universidade da Coruña, Campus da Zapateira, s/n, 15071 A Coruña, Spain

  DOI: 10.1002/ejic.200400331

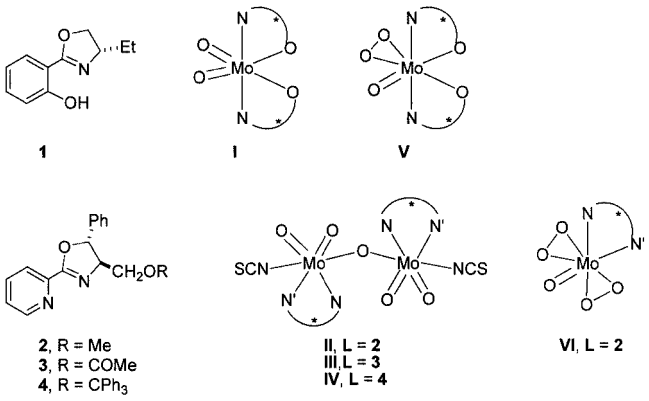


Figure 1. Oxazoline chiral ligands **1**−**4** and oxomolybdenum complexes **I**−**VI**

ation processes. Related structural studies, especially in solution, afforded new insight into the nature of the catalytic species involved.

Results and Discussion

Dimetallic Dioxomolybdenum Complexes II−IV

Dimetallic bis(oxazolinylpyridine)dioxo(μ-oxo)dimolybdenum(VI) complexes **II**−**IV** with oxazolinylpyridines of the general formula (μ-O)[MoO_2(NCS)(κ²-*N*,*N*-**L**)]₂ (**L** = **2**−**4**) were prepared according to the methodology previously described (Scheme 1, a).[13] A dichloromethane solution of the ligand **2**−**4** was added to an acidic aqueous solution of $Na_2MoO_4{\cdot}2H_2O$ and KSCN under phase-transfer conditions, affording the corresponding complexes in good yields (ca. 70%). Using the same conditions, the analogous complexes containing bis(oxazoline) ligands could not be isolated due to the oxazoline moiety decomposing to give amide derivatives. Modifications of the experimental conditions (higher pH values, different solution concentrations) were also unsuccessful.[14]

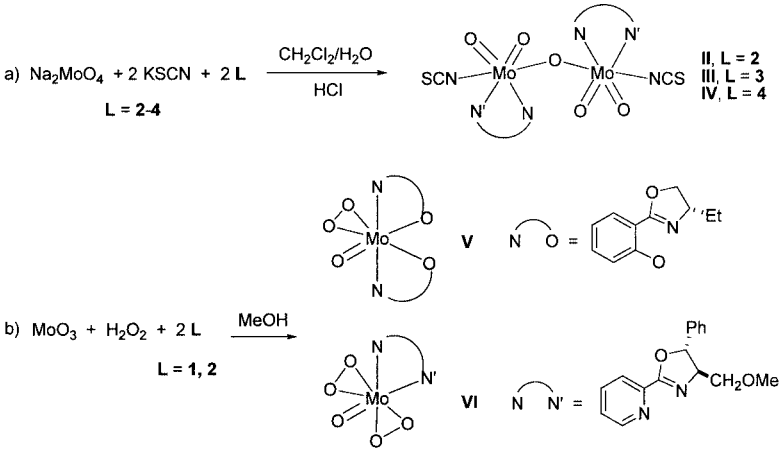
The IR spectra of **II**−**IV** show the characteristic functional group absorptions: a very strong band for NCS at ca. 2050 cm^{-1}, 1658 cm^{-1} for the oxazoline imine bond, two strong bands at 906 and 941 cm^{-1} for Mo=O as well as 772 cm^{-1} for the μ-oxo moiety (Mo−O−Mo). In the positive FAB-MS spectra, despite the absence of the parent ion, fragments such as $[Mo_2O_5(NCS)\mathbf{L}_2]^+$, $[Mo_2O_4(NCS)\mathbf{L}]^+$ and $[Mo_2O(NCS)\mathbf{L}]^+$ indicate the dimetallic nature of the complexes.

Efforts to grow single crystals were unsuccessful, probably due to the existence of some isomers (see below).

Studies in solution showed the presence of several species and the 2D NOESY spectra revealed exchange signals among them all. In the case of **II**, the signals were well enough separated to allow us to suggest the presence of at least six species (relative ratios 8.0:5.6:3.3:2.5:1.6:1) in $CDCl_3$. The most abundant isomer (ca. 40%) shows two equivalent oxazolinylpyridine fragments. The other isomers, however, show signals indicating that the two bidentate ligands are not chemically equivalent. In the case of symmetrical ligands, as in the 4,4′-disubstituted bipyridine compound (μ-O)[MoO_2(NCS)(4,4′-*tert*-butyl-2,2′-bpy)]₂, two isomers were formed depending on the Mo−O−Mo bridge angle (180° and ca. 156°, respectively, relative ratios 44:56).[13] The formation of more than two species would be expected for nonsymmetrical oxazolinylpyridines **2**−**4** and the major isomer exhibiting the symmetrical structure must correspond to the conformer with an Mo−O−Mo angle of 180°. In Figure 2, the arrangements of the three nonequivalent isomers are depicted with an Mo−O−Mo bridge angle of 180° and where the isocyanate ligand is opposite to the bridging oxygen atom. In addition, the corresponding isomers with an Mo−O−Mo angle less than 180°, could also be expected.

Monometallic Oxo(peroxo)molybdenum Complexes V, VI

New seven-coordinate monometallic oxo(peroxo)molybdenum(VI) complexes **V**, **VI** containing chiral oxazoline ligands were prepared by previously reported methods.[15] For the anion of **1**, an oxo(peroxo) compound with two bidentate N,O ligands, $[MoO(O_2)(\kappa^2\text{-}N,O\text{-}\mathbf{L})_2]$ (**V**), was isolated while for the oxazolinylpyridine **2**, the oxobis(peroxo)



Scheme 1. Synthesis of dioxo(μ-oxo) dimetallic (**II**−**IV**) (a) and oxo(peroxo) monometallic (**V** and **VI**) (b) molybdenum(VI) complexes

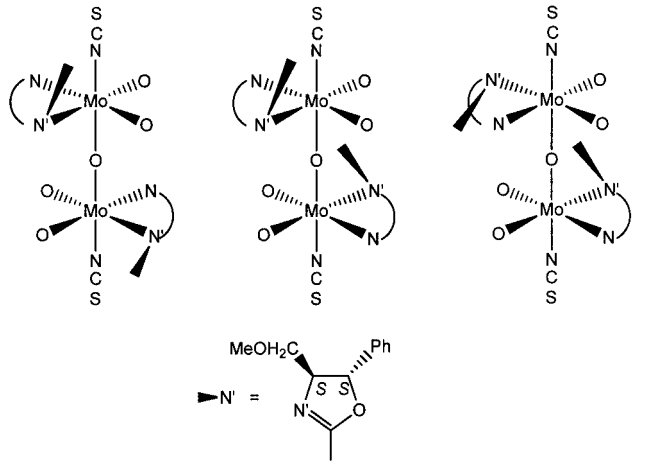


Figure 2. Isomers of dimetallic complex **II** containing the pure chiral oxazolinylpyridine ligand **2**, with an Mo−O−Mo angle of ca. 180°

complex $[MoO(O_2)_2(\kappa^2\text{-}N,N\text{-}\mathbf{2})]$ (**VI**) was produced (Scheme 1, b).

MoO_3 was dissolved in H_2O_2 (30%) to prepare an aqueous solution of $[Mo(O)(O_2)_2(H_2O)_2]$ (pH = 4). A methanol solution of the oxazoline **1**−**2** was then added and after addition of diethyl ether, **V** and **VI** were isolated as yellow solids, both stable in the solid state and in solution. No corresponding amide derivatives of the oxazolines were observed under these conditions. Attempts to isolate the oxo(peroxo) species **V** by perhydrolysis of **I** were unsuccessful.

In the solid state, the IR spectra of **V** and **VI** show two characteristic strong absorption bands at 962 (Mo=O) and 865−863 (O−O) cm^{-1}, as well as a very strong band at 1636−1630 (C=N) cm^{-1} corresponding to the oxazoline imine bond.

Single crystals of **V** and **VI** were obtained from dichloromethane/diethyl ether solutions (Figure 3). In Table 1, selected bond lengths and angles are collected. In **V**, the molybdenum atom is heptacoordinated by an oxo, a peroxo and two bidentate anionic phenolate oxazoline ligands. The geometry around the metal atom can be described as pseudo-pentagonal bipyramidal with the axial sites occupied by the oxo group O(1) and one of the phenolate oxygen atoms O(4). Thermal disorder is present around the Mo−oxo unit with high anisotropic parameters. The disorder was modelled with the two positions O(1A) and O(1B) having partial occupancies of 0.46(3) and 0.54(3), respectively. The peroxo bond O(2)−O(3) (1.3 Å) is shorter than usual (ca. 1.4−1.5 Å). This fact can be attributed to the relatively high thermal parameter for O(2) (anisotropic displacement parameter 0.148) compared with those of the phenolate and oxazolinyl oxygen atoms (0.05−0.07). Consequently, the distance is inaccurate. The remaining coordinating atoms are located in the equatorial plane in an almost coplanar arrangement, as indicated by the dihedral angles: N(1)−O(6)−N(2)−O(3) 4.60°, O(6)−N(2)−O(3)−O(2) 0.93°, N(2)−O(3)−O(2)−N(1) 5.43°, O(3)−O(2)−N(1)−O(6) 8.16° and O(2)−N(1)−O(6)−N(2) 6.11°. The other bond lengths and angles are similar to those in the only related published complex $[MoO(O_2)(8\text{-quinolate})_2]$.[16] In our case, the two nitrogen atoms are located almost opposite to each other [N(1)−Mo(1)−N(2) = 158.96°], while in the example reported in ref.[16], the two nitrogen atoms are vicinal (N−Mo−N = 81.91°).

In structure **VI**, the molybdenum atom is also heptacoordinated by an oxo group, two peroxo moieties and one bidentate oxazolinylpyridine **2** and the geometry around the metal atom can also be described as pseudo-pentagonal bipyramidal, with the axial sites occupied by the oxo group O(1) and the nitrogen atom from the pyridine moiety of the oxazoline ligand N(1). The remaining coordinating atoms are located in the equatorial plane in a nearly coplanar distribution, as indicated by the dihedral angles O(3)−O(2)−O(4)−O(5) 0.991°, N(2)−O(5)−O(4)−O(2) 1.596°, O(2)−O(3)−N(2)−O(5) 3.143° and O(3)−N(2)−O(5)−O(4) 2.460°. These angles are similar to other heptacoordinate oxobis(peroxo)molybdenum complexes containing bipyridine[17,18] and pyrazolylpyridine[19−21] derivatives. In the X-ray diffraction studies of the N,N-unsymmetrical ligands, the pyridine fragment is in an equatorial position while in **VI** it is axial. Intramolecular non-bonding O···H distances are longer than 3 Å.

The ^1H NMR spectrum of a freshly prepared solution of **V** in $CDCl_3$ revealed that the two anionic N,O-bidentate moieties are nonequivalent. A second set of signals appeared after approximately 12 h resulting in a relative ratio between the two molybdenum species of ca. 10:1. In deuterated acetone, the formation of the second species is favoured (relative ratio 4:1) and no changes were observed even after several days. This solvent dependence turned out to be similar to that observed for the analogous dioxomolybdenum complex **I** where partial decoordination of the oxazoline ligand takes place in coordinating solvents.[9]

For the major compound, important differences in the chemical shifts were observed. Compared with the free oxazoline [δ(H) = 4.10 ppm] the stereo-centre proton signal shifted remarkably downfield [δ(H) = 5.06 and 5.73 ppm]. This deshielding can be attributed to interaction with the oxo and peroxo groups, as shown by the average interatomic distances H(8A)···O=Mo and H(19A)···O_2−Mo from the crystallographic data, ca. 2.85 and 2.25 Å, respectively.

NMR studies of **VI** in solution clearly indicated only one compound in coordinating solvents. The chemical shifts of the oxazoline protons moved downfield (Δδ = 0.2−0.7 ppm) relative to those of the free oxazoline **2**. The coordination of the oxazolinylpyridine ligand is limited to the pyridine nitrogen atom located in an axial position opposite to the strong *trans*-directing oxo group in agreement with the X-ray study, although the thermodynamically favoured isomer should bear the poorer σ-donor moiety *trans* to the oxo group. In addition, the stereochemical behaviour is similar to that observed for oxobis(peroxo)molybdenum complexes with *N*,*N*-pyrazolylpyridines,[22] but oxazolinylpyridine dissociation was not observed.

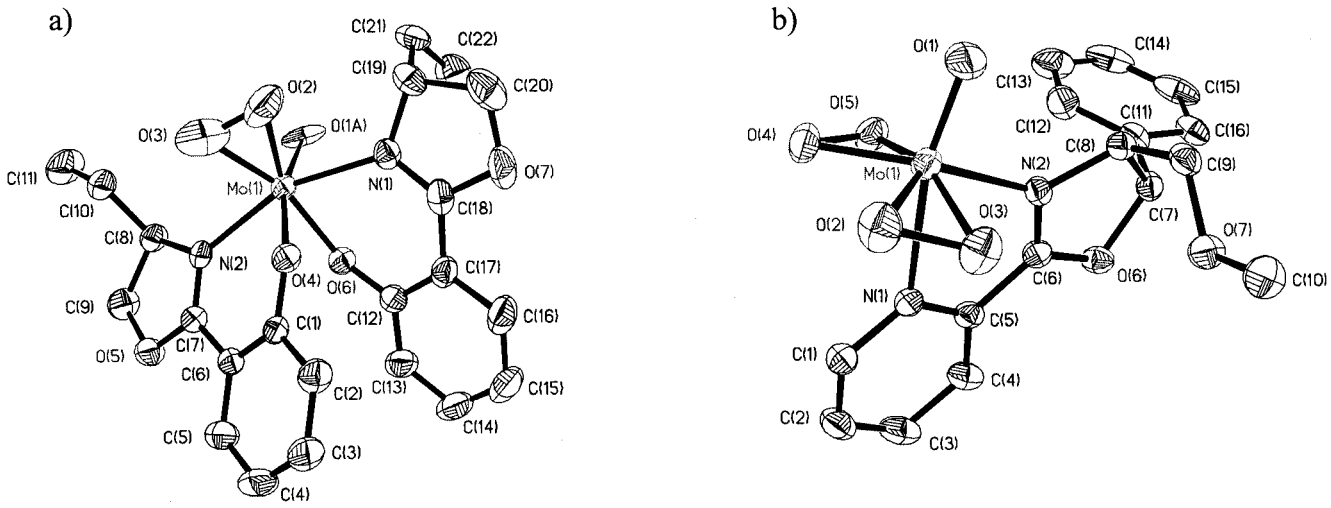


Figure 3. ORTEP diagrams of the molecular structures of **V** (a) and **VI** (b); hydrogen atoms are omitted for clarity

Table 1. Selected bond lengths [Å] and bond angles [°] for **V** and **VI** (with esds in parentheses)

	V	**VI**
Mo−O(1)	1.732(16)[a]	1.674(2)
Mo−O(2)	1.946(6)	1.912(2)
Mo−O(3)	1.979(7)	1.940(2)
Mo−O(4)	2.044(3)	1.928(2)
Mo−O(5)	–	1.9460(19)
Mo−O(6)	2.029(3)	–
Mo−N(1)	2.161(4)	2.427(2)
Mo−N(2)	2.167(3)	2.1524(18)
O(2)−O(3)	1.312(7)[b]	1.459(3)
O(4)−O(5)	–	1.474(3)
O(1)−Mo−O(4)	160.35(6)[a]	105.66(12)
O(1)−Mo−N(1)	105.3(5)[a]	164.45(10)
O(1)−Mo−N(2)	94.7(6)[a]	94.17(10)
O(1)−Mo−O(3)	101.7(4)[a]	102.96(11)
O(1)−Mo−O(5)	–	101.78(12)
N(1)−Mo−N(2)	158.96(13)	70.34(7)
O(4)−Mo−O(6)	81.16(12)	–
O(4)−Mo−O(5)	–	44.73(8)
O(6)−Mo−N(1)	80.23(14)	–
O(2)−Mo−O(1)	100.9(4)[a]	106.07(12)
O(2)−Mo−O(3)	39.1(2)	44.52(10)
N(1)−Mo−O(6)	80.34(13)	–
O(6)−Mo−N(2)	83.34(13)	–
N(2)−Mo−O(3)	80.4(2)	86.97(9)

[a] Average bond length and angle. [b] See X-ray discussion in the text.

Olefin Epoxidation Catalysed by Oxomolybdenum Complexes

The dioxo mono- and dimetallic complexes **I** and **II**, respectively, were tested as catalytic precursors for the epoxidation of cyclooctene (**5**), norbornene (**6**) and (*R*)-limonene (**7**), using *t*BuOOH in water as the oxidant at room temperature (Scheme 2). When reactions were performed using *t*BuOOH in decane, lower conversions were obtained. Catalytic reactions were carried out with and without solvent (toluene). Table 2 lists the catalytic results. In the case of **I**, activities were higher in the presence of solvent (Entries 1, 3, 5 and 6) but for **II** these differences were not significant (Entries 2, 4, 7 and 8). For both systems, cyclooctene oxide **8** and *exo*-norbornene oxide **9** were the only products obtained and the monometallic system **I** was more active (up to 57% conversion, Entry 3) than dimetallic **II** (Entries 1 and 3 versus 2 and 4). In the case of limonene oxidation, a mixture of products was detected, *trans*/*cis*-limonene oxide (**10**), the corresponding double epoxide (**11**) and alcohols (Scheme 2). Activity (substrate conversion) and chemoselectivity (ratio **10**/**11**) are almost the same for both catalytic systems (Entries 5−8). Ring epoxide opening to afford alcohols was lower for **I** than for **II** (alcohols/epoxide = 0−0.1 for **I** and 0.2−0.5 for **II**) (Entries 5 and 6 versus 7 and 8). An outstanding diastereoisomeric induction was observed for **10** when **II** was used (*trans*/*cis*-**10** up to 9:1 for 77% of olefin conversion, Entry 8) but no discrimination occurred with **I** (Entries 5 and 6).

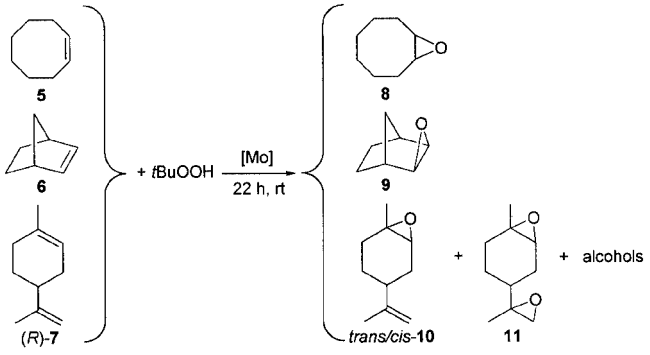
The absence of exocyclic oxide formation suggests that the double epoxide **11** is probably produced by epoxidation of **10**. When *trans*/*cis*-**10** (ratio ca. 1:1) was used as the substrate and **II** as the catalyst, under the same experimental conditions, a 45% conversion to **11** and alcohols (**11**/alcohols ≈ 4:1) was obtained (Scheme 3). The remaining **10**, enriched in one of the diastereoisomers (relative ratio *trans*/*cis*-**10** > 98:2), indicates that *cis*-**10** reacts faster than *trans*-**10**. However, when monometallic complex **I** was used as a catalytic precursor, no kinetic resolution occurred.

Oxo(peroxo)molybdenum species are known key intermediates in epoxidation processes. The mono- and bis-

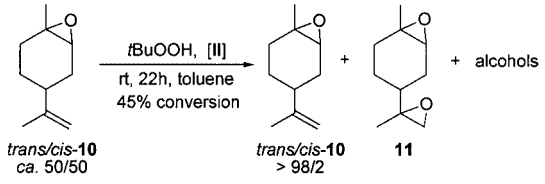
Table 2. Results of epoxidation of olefins **5**−**7** with *t*BuOOH as an oxidant catalysed by molybdenum complexes **I**, **II**, **V** and **VI** (Scheme 2)

Entry[a]	Complex	Olefin	Conv. (%)[b]	**10** (%)[c] (*trans*/*cis*)	**11** (%)[d]	Alcohols (%)[d]	Alcohols/epoxides
1	**I**	**5**	52 (27) (41)	−	−	−	−
2	**II**	**5**	36 (40) (8)	−	−	−	−
3	**I**	**6**	57 (39) (40)	−	−	−	−
4	**II**	**6**	34 (20) (20)	−	−	−	−
5	**I**	(*R*)-**7**	62 (35)	54 (54:46)	2.0	6.0	0.1
6[e]	**I**	(*R*)-**7**	58 (35)	54 (60:40)	4.0	0	0
7	**II**	(*R*)-**7**	64 (46)	50 (80:20)	4.0	10.0	0.2
8[e]	**II**	(*R*)-**7**	77 (45)	45 (90:10)	6.0	26.0	0.5
9	**V**	**5**	95 (92) (83)	−	−	−	−
10	**VI**	**5**	15 (38)	−	−	−	−
11	**V**	(*R*)-**7**	79	62 (60:40)	2.0	15.0	0.2
12	**VI**	(*R*)-**7**	22	22 (50:50)	0	0	0

[a] Catalytic conditions: 0.025 mmol of Mo (complexes **I**, **II**, **V** and **VI**), 1 mmol olefin (**5**−**7**) and 1.5 mmol of *t*BuOOH (8 M in water) in 1 mL of toluene at room temp. for 22 h; 0.2−0.4 mmol of undecane (as external standard) was used to quantify the catalytic reaction. [b] Conversion percentage based on the substrate determined by GC; in parentheses is the conversion obtained without solvent; in italics the conversions obtained using *t*BuOOH in decane (5.5 M). [c] In parentheses, the ratio of *trans*/*cis* of endocyclic epoxide **10**. [d] Determined by GC. [e] Reaction carried out without solvent.



Scheme 2. Cyclooctene (**5**), norbornene (**6**) and (*R*)-limonene (**7**) epoxidation catalysed by **I**, **II**, **V** and **VI** using *t*BuOOH as an oxidant; olefin/*t*BuOOH/Mo = 40:60:1



Scheme 3. *trans*/*cis*-Limonene oxide (**10**) epoxidation catalysed by **II** using *t*BuOOH as an oxidant; olefin/*t*BuOOH/Mo = 40:60:1

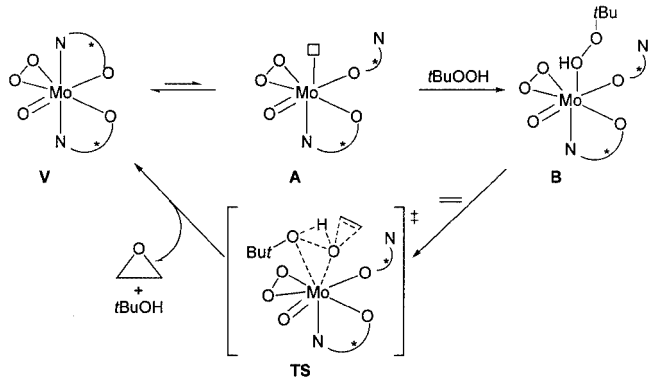
(peroxo) complexes **V** and **VI** were tested for oxidation of **5** and (*R*)-**7**. It was found that **V** was the most active of all systems studied (Entries 9 and 11) achieving 95% cyclooctene conversion (Entry 9). The higher activities observed for oxo(peroxo) species **V** than for the dioxo compound **I** suggest that the former is the catalytically active species and **I** is its precursor. On the contrary, **VI** gave the lowest conversions (Entries 10 and 12). Similar to the dioxo monometallic complex **I**, diastereoisomeric induction of (*R*)-limonene did not take place for either **V** or **VI**.

Mechanistic Aspects of Olefin Epoxidation

The structural studies carried out provided evidence of a certain relationship between the lability of the molybdenum centre and catalytic olefin epoxidation. Despite heptacoordinated oxobis(peroxo)molybdenum complexes having been reported to be fairly good epoxidation catalysts, the unexpected low activity [in the oxidation of cyclooctene and (*R*)-limonene] observed for **VI** can be attributed to the nonlability of the oxazolinylpyridine ligand, as observed by NMR spectroscopy (see above). However, in the case of **V**, the high activity obtained is in accordance with partial decoordination of the *N*,*O*-oxazolinylphenolate ligand, already observed for its precursor **I**[9] and for oxobis(peroxo) Thiel-type complexes.[19−22] The ability to generate a coordination vacancy at the molybdenum atom can then be responsible for the differences in the catalytic behaviour of **V** and **VI**. Furthermore, the remarkably higher activity obtained with **II** compared with **VI**, with both systems containing the nonlabile bidentate ligand **2**, is due to the facile formation of a vacant site in **II** by isothiocyanate dissociation. Thus, metallic species with unsaturated coordination environments will favour either the olefin or the oxidant to approach the metal. With regards to the equimolar *trans*/*cis*-**10** mixture obtained in the epoxidation of (*R*)-limonene using monometallic catalysts, the species directly coordinated to the molybdenum centre is probably *t*BuOOH instead of the olefin.

Information derived from NMR experiments and catalytic reactivity patterns allows us to propose the mechanism shown in Scheme 4. The oxo(peroxo)molybdenum species **V** can easily form a vacant site due to the hemilabile nature of the oxazolinylphenolate ligand (**A**). Further coordination of *t*BuOOH (**B**) leads to the formation of a transition state (**TS**), in which the olefin approaches towards the *tert*-butyl peroxide fragment, producing the epoxide and concomitant elimination of *tert*-butyl alcohol, the active catalytic species **V** being regenerated.

On the other hand, the unexpected selectivity observed with the dimetallic catalytic system **II** in both oxidations, (*R*)-limonene (**7**) (Entries 7 and 8, Table 2) and limonene epoxide **10** (Scheme 3), can only just be explained by the



Scheme 4. Mechanistic proposal for olefin epoxidation catalysed by seven-coordinate molybdenum species containing hemilabile ligands

mechanism described. Nevertheless, as stated above, the nonlability of the oxazolinylpyridine ligand and the presence of a vacant site can favour the direct olefin coordination to the metal atom. Stereoselectivity control in the organic process is then possible.

Further reactivity studies with dimetallic molybdenum species involved in catalytic olefin epoxidations are in progress.

Experimental Section

General Remarks: Solvents were purified by standard procedures and distilled under nitrogen. $Na_2MoO_4{\cdot}2H_2O$ (Probus), MoO_3 (Strem), aqueous *t*BuOOH (8 M; Fluka), *t*BuOOH in decane solution (5.5 M; Fluka), cyclooctene (Fluka), norbornene (Aldrich) and (*R*)-limonene (Aldrich) were used as purchased. Ligands **1**,[23] **2**−**4**[24,25] and complex **I**[9] were prepared as described previously. NMR spectra (in $CDCl_3$) were recorded with Bruker Avance600, Varian XL-500, Varian Gemini or Bruker DRX 250 spectrometers. Chemical shifts are reported downfield from standards. IR spectra were recorded with a Nicolet 520 FT-IR or a Bruker IFS 55 FTIR spectrometer. FAB mass spectra were obtained with a Micromass VG-Quattro instrument. The GC-MS analyses were performed with a Hewlett−Packard 5890 Series II gas chromatograph (50 m Ultra 2 capillary column) interfaced with a Hewlett−Packard 5971 mass-selective detector. Elemental analyses were carried out by the Serveis Cientifico-Tècnics de la Universitat de Barcelona with an Eager 1108 microanalyser.

μ-Oxobis{[(3′*S*,4′*S*)-2-(3′,4′-dihydro-4′-methoxymethyl-2′-oxazolyl-3′-phenyl)pyridine-*N*,*N*](isothiocyanato)dioxomolybdenum(VI)} (II): HCl (1 M 1.7 mmol, 1.7 mL) was slowly added, with stirring, to a mixture of aqueous solutions (10 mL) of $Na_2MoO_4{\cdot}2H_2O$ (100 mg, 0.413 mmol) and KNCS (160 mg, 1.652 mmol). After 15 min, the oxazolinylpyridine **2** (110.8 mg, 0.413 mmol) in CH_2Cl_2 (20 mL) was added to the yellow solution and vigorously stirred for 45 min. The organic layer was extracted, washed with water (3 × 10 mL) and dried with Na_2SO_4. The solvent was removed under reduced pressure. The solid obtained was washed with diethyl ether (3 × 20 mL) and dried under vacuum. Yield: 0.161 g (77%). $C_{34}H_{32}Mo_2N_6O_9S_2$ (924.68): calcd. C 43.68, H 3.46, N 9.09, S 6.93; found C 43.62, H 3.29, N 8.90, S 6.84. MS (FAB positive): *m*/*z* = 867 [M − NCS]. IR (KBr): $\tilde{\nu}$ = 2045 (st, C=N_{NCS}), 1658 (st, C=N), 941 and 906 (Mo=O) cm^{-1}. ^1H NMR (600 MHz): δ_{major} = 8.87 (d, *J* = 4.8 Hz, 1 H), 8.18 (pt, *J* = 7.8 Hz, 1 H), 8.06 (d, *J* = 7.6 Hz, 1 H), 7.4−7.2 (m, 5 H), 6.02 (d, *J* = 7.0 Hz, 1 H), 4.45 (m, 1 H), 3.87 (m, 1 H), 3.78 (dd, *J* = 10.0, 3.4 Hz,1 H), 3.40 (s, 3 H) ppm.

μ-Oxobis{[(3′*S*,4′*S*)-2-(4′-acetoxymethyl-3′,4′-dihydro-2′-oxazolyl-3′-phenyl)pyridine-*N*,*N*](isothiocyanato)dioxomolybdenum(VI)} (III): An analogous procedure to that described for the preparation of **II** was used, replacing **2** with **3**.Yield: 0.443 g (75%). $C_{38}H_{36}Mo_2N_6O_{11}S_2$ (1008.37): calcd. C 44.02, H 3.48, N 8.11, S 6.18; found C 44.50, H 3.65, N 7.80, S 5.94. MS (FAB positive): *m*/*z* = 1010 [M], 922 [M − NCS − 2 O]. IR (KBr): $\tilde{\nu}$ = 2056 (st, C=N_{NCS}), 1658 (st, C=N) and, 940 and 910 (Mo=O) cm^{-1}.

μ-Oxobis{[(3′*S*,4′*S*)-2-(3′,4′-dihydro-2′-oxazolyl-3′-phenyl-4′-tritylmethyl)pyridine-*N*,*N*](isothiocyanato)dioxomolybdenum(VI)} (IV): An analogous procedure to that described for the preparation of **II** was used, replacing **2** with **4**. Yield: 0.302 g (68%). $C_{70}H_{56}Mo_2N_6O_9S_2$ (1381.26): calcd. C 60.87, H 4.06, N 6.09, S 4.64; found C 59.75, H 3.98, N 5.99, S 5.03. MS (FAB positive): *m*/*z* = 780 [M − NCS − 3 O − **4**]. IR (KBr): $\tilde{\nu}$ = 2043 (st, C=N_{NCS}), 1658 (st, C=N) and, 942 and 911 (Mo=O) cm^{-1}.

Bis[(4′*R*)-2-(4′-ethyl-3′,4′-dihydro-2′-oxazolyl)phenolato-*N*,*O*]oxo(peroxo)molybdenum(VI) (V): MoO_3 (0.285 g, 1.980 mmol) was added in portions to an aqueous H_2O_2 solution (30%, 5 mL) at room temperature. The mixture was stirred for 20 min and warmed to 40 °C for 40 min. The reaction mixture was filtered, the yellow solution was cooled to 10 °C and a solution of **1** (0.384 g, 2.00 mmol) in CH_3OH was added. The mixture was stirred at 20 °C for 30 min and then at 0 °C for 16 h. It was concentrated under reduced pressure to approximately 5 mL and diethyl ether was added (20 mL). The yellow precipitate obtained was filtered and recrystallized from CH_2Cl_2/diethyl ether (3:1). Yield: 0.405 g (39%). M.p. 197 °C. $C_{22}H_{24}MoN_2O_7$ (524.38): calcd. C 50.39, H 4.61, N 5.34; found C 50.34, H4.85, N 5.17. MS (FAB positive): *m*/*z* = 525. IR (KBr): $\tilde{\nu}$ = 1630 (st, C=N), 962 (st, Mo=O), 865 (st, O−O), 758 (asymm. st Mo−O), 582 (symm. st Mo−O) cm^{-1}. ^1H NMR (500 MHz): δ_{major} = 7.68 (dd, *J* = 8.5, 1.5 Hz, 1 H), 7.53 (dd, *J* = 8.0, 1.5 Hz, 1 H), 6.93 (m, 1 H), 6.88 (m, 1 H), 6.56 (m, 2 H), 6.04 (dd, *J* = 8.5, 0.5 Hz, 1 H), 5.77 (dd, *J* = 8.5, 0.5 Hz, 1 H), 5.73 (m, 1 H), 5.06 (m, 1 H), 4.92 (dd, *J* = 8.5, 6.5 Hz, 1 H), 4.88 (dd, *J* = 8.5, 5.5 Hz, 1 H), 4.60 (dd, *J* = 8.5, 5.5 Hz, 2 H), 4.52 (dd, *J* = 8.5, 6.5 Hz, 1 H), 2.45 (m, 1 H), 2.20 (m, 1 H), 2.15 (m, 1 H), 2.02 (m, 1 H); 1.07 (t, *J* = 7.5 Hz,, 3 H), 1.01 (t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR (75 MHz): δ = 167.6 (C=N), 167.4 (C=N), 166.2 (C), 164.0 (C), 135.4 (CH), 135.0 (CH), 129.1 (CH), 128.5 (CH), 120.9 (CH), 120.0 (CH), 117.8 (CH), 117.5 (CH), 112.7 (C−O), 111.3 (C−O), 73.1 (CH_2−O), 72.7 (CH_2−O), 70.0 (CH), 64.6 (CH), 28.1 (CH_2), 26.5 (CH_2), 9.1 (CH_3), 8.2 (CH_3) ppm. δ_{minor} = 8.08 (dd, *J* = 8, 1 Hz, 1 H), 7.78 (dd, *J* = 8 Hz, 1 H), 7.65 (m, 1 H), 7.50 (m, 1 H), 7.36 (pt, *J* = 7.5 Hz 1 H), 7.05 (m, 2 H), 6.11 (d *J* = 8.5 Hz, 1 H), 4.69 (pt, *J* = 10 Hz, 1 H), 4.44 (dd, *J* = 8.5, 5 Hz, 1 H), 4.28 (pt, *J* = 10 Hz, 1 H), 3.77 (dd, *J* = 5.0, 11. 5 Hz, 1 H), 1.90 (m, 2 H), 0.95 (t, *J* = 7.5 Hz, 3 H), 0.88 (t, *J* = 7.5 Hz, 3 H) ppm.

[(3′*S*,4′*S*)-2-(3′,4′-Dihydro-4′-methoxymethyl-2′-oxazolyl-3′-phenyl)pyridine-*N*,*N*]oxobis(peroxo)molybdenum(VI) (VI): MoO_3 (0.252 g, 1.75 mmol) was added in portions to an aqueous H_2O_2 solution (30%, 5 mL). The mixture was stirred for 20 min and warmed to 40 °C for 4 h. The reaction mixture was filtered and to the yellow solution was added **2** (0.470 g, 1.75 mmol) in CH_3OH (20 mL). The mixture was stirred at room temperature for 1 h and then concentrated under reduced pressure to 1 mL. Ethanol was

Table 3. Crystal data for **V** and **VI**

	V	**VI**
Empirical formula	$C_{22}H_{24}MoN_2O_7$	$C_{16}H_{16}MoN_2O_7$
Formula mass	524.37	444.25
Crystal size [mm]	0.50 × 0.16 × 0.10	0.27 × 0.10 × 0.08
Temperature [K]	298(2)	298(2)
Crystal system	orthorhombic	monoclinic
Space group	*P*2(1)2(1)2(1)	*P*2(1)
a [Å]	6.7608(8)	7.2720(4)
b [Å]	9.9119(11)	14.6377(8)
c [Å]	33.456(4)	8.4005(4)
β [°]	90	90.6780(10)
V [Å^3]	2242.0(4)	894.13(8)
Z	4	2
Density (calculated) [Mg·m^{-3}]	1.554	1.650
Absorption coefficient [mm^{-1}]	0.631	0.774
θ range for data collection [°]	2.14−26.38	2.42−28.28
Reflections collected	12971	5751
Data/restraints/parameters	4560/0/299	3392/1/235
Independent reflections	4560 [*R*(int) = 0.0294]	3392 [*R*(int) = 0.0162]
Max./min. transmission	0.9396/0.7433	0.9407/0.8182
Final *R*(int) [$I > 2\sigma(I)$][a]	*R*1 = 0.0388, *wR*2 = 0.1020[b]	*R*1 = 0.0211, *wR*2 = 0.0526[b]
R int (all data)	*R*1 = 0.0482, *wR*2 = 0.107	*R*1 = 0.0227, *wR*2 = 0.0535
GOF on F^2	1.061	1.025
Absolute structure parameter	−0.02(5)	0.00(3)
Largest diff. peak/hole [e·Å^{-3}]	0.565/−0.481	0.201/−0.490

[a] $R1 = \Sigma||F_o| - |F_c||$ and $wR2 = \{\Sigma[w(F_o^2 - F_c^2)]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [b] The weighting scheme employed was $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$ and $P = (|F_o|^2 + 2|F_c|^2)/3$.

added (2 × 20 mL) and removed each time. The yellow solid obtained was recrystallized from CH_2Cl_2/hexane (9:1). Yield: 0.234 g (30%). M.p. 146 °C. $C_{16}H_{16}MoN_2O_7$ (444.25): calcd. C 43.26, H 3.63, N 6.31; found C 47.28, H 5.05, N 6.31. MS (ES): *m*/*z* = 445 [M + 1], 415 [M − O_2]. IR (KBr): ṽ = 1636 (st, C=N), 962 (st, Mo=O), 863 (st, O−O), 769 (asymm. st Mo−O) and 581 (symm. st Mo−O) cm^{-1}. ^{1}H NMR (400 MHz): δ = 8.39 (pd, *J* = 5.2 Hz, 1 H), 7.94 (m, *J* = 1.6 Hz, 8 Hz, 2 H), 7.55 (m, *J* = 2 Hz, 1.6 Hz, 1 H), 7.49 (s, 5 H), 6.34 (d, *J* = 6.8 Hz, 1 H), 5.01 (m, 1 H), 4.30 (dd, *J* = 3.6 Hz; *J* = 10.8 Hz, 1 H), 3.98 (dd, *J* = 2.8 Hz; *J* = 10.8 Hz, 1 H), 3.57 (s, 3 H) ppm. ^{13}C NMR (75 MHz): δ = 169.8 (C=N), 148.0 (CH), 139.2 (CH), 139.1 (C), 135.9 (C), 130.4 (CH), 129.6 (CH), 129.3 (CH), 126.5 (CH), 124.6 (CH), 89.9 (CH), 73.4 (CH), 70.7 (CH_2−O), 59.6 (CH_3−O) ppm.

Molybdenum-Catalysed Olefin Epoxidation: The precursor (0.025 mmol of complex: 12.7 mg for **I**, 11.6 mg for **II**, 13.1 mg for **V** and 11.1 mg for **VI**) was dissolved in toluene (1 mL). The olefin (1 mmol, 110 mg for **5**, 94 mg for **6** and 139 mg for **7**) was added, followed by a *tert*-butyl hydroperoxide aqueous solution (8 M, 0.19 mL, 1.50 mmol). The mixture was stirred at room temperature for 22 h and then quenched by addition of ethyl acetate and filtered through silica. Undecane was added as an external standard (0.2−0.4 mmol). Analyses of organic products were performed by gas chromatography. Catalytic reactions were also performed without solvent according to the above mentioned experimental procedure.

X-ray Crystallographic Studies: Single crystals were grown by allowing diethyl ether to diffuse into a dichloromethane solution. The crystal data for **V** and **VI** were collected using a Bruker SMART CCD based diffractometer operating at room temperature. Intensities were collected with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) generated at 50 kV and 30 mA, using the ω/2θ scan technique. A total of 1271 frames of intensity data were collected over a hemisphere of the reciprocal space by combination of three exposure sets. Each frame covered 0.3° in ω and the first 50 frames were recollected at the end of data collection to monitor crystal decay. The crystals used for the diffraction studies showed no decomposition during data collection. The crystallographic data for **V** and **VI** are summarised in Table 3. Absorption corrections were applied using the SADABS programme.[26] The structures were solved using the Bruker SHELXTL-PC software by direct methods and refined by full-matrix least-squares methods on F^2.[27] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined using the riding mode. CCDC-236207 (**V**) and -236208 (**VI**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We would like to thank the Spanish Ministerio de Ciencia y Tecnología (BQU 2001-3358), Generalitat de Catalunya and the Decanato de Investigación y Desarrollo (Universidad Simón Bolívar) for financial support. The authors thank Dr. Xavier Santos for the GC analysis. J. B. thanks the Universitat de Barcelona for a two-year pre-doctoral grant.

[1] R. H. Holm, *Coord. Chem. Rev.* **1990**, *100*, 183−221 and references cited therein.
[2] R. C. Maurya, D. D. Mishra, S. N. Rao, R. Verma, N. N. Rao, *Ind. J. Chem.* **1997**, *36*, 599.
[3] H. Mimoun, I. Seree de Roch, L. Sajus, *Tetrahedron* **1970**, *26*, 37−50.

[4] H. Mimoun, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 734−750.
[5] K. B. Sharpless, J. M. Townsen, D. R. Williams, *J. Am. Chem. Soc.* **1972**, *94*, 295−296.
[6] K. A. Jørgensen, R. Hoffmann, *Acta Chem. Scand., Ser. B* **1986**, *40*, 411−419.
[7] P. Macchi, A. J. Schultz, F. K. Larsen, D. B. Iversen, *J. Phys. Chem. A* **2001**, *105*, 9231−9242.
[8] A. Hroch, G. Gemmecker, W. R. Thiel, *Eur. J. Inorg. Chem.* **2000**, 1107−1114.
[9] M. Gómez, S. Jansat, G. Muller, G. Noguera, H. Teruel, V. Moliner, E. Cerrada, M. Hursthouse, *Eur. J. Inorg. Chem.* **2001**, 1071−1076.
[10] M. Gómez, G. Muller, M. Rocamora, *Coord. Chem. Rev.* **1999**, *193−195*, 769−835.
[11] G. Helmchen, A. Pfaltz, *Acc. Chem. Res.* **2000**, *33*, 336−345.
[12] *Catalytic Asymmetric Synthesis* (Ed.; I. Ojima), 2nd ed., John Wiley & Sons, New York, **2000**.
[13] H. Arzoumanian, R. Bakhtchadjian, G. Agrifoglio, H. Krentzien, J.-C. Daran, *Eur. J. Inorg. Chem.* **1999**, 2255−2259.
[14] Bis(oxazolines) used were: 1,2-bis[(4*R*)-4-ethyl-Δ^2-1,3-oxazolin-2-yl)]benzene and 1,2-bis[(4*R*)-4-ethyl-Δ^2-1,3-oxazolin-2-yl)]ethane: M. Gómez, S. Jansat, G. Muller, M. A. Maestro, J. Mahía, M. Font-Bardía, X. Solans, *J. Chem. Soc., Dalton Trans.* **2001**, 1432−1439.
[15] R. J. Cross, P. D. Newman, R. D. Peacock, D. Stirling, *J. Mol. Catal. A: Chem.* **1999**, *144*, 273−284.
[16] R. Bandyopadhyay, S. Biswas, S. Guha, A. K. Mukherjee, R. Bhattacharyya, *Chem. Commun.* **1999**, 1627−1628.
[17] E. O. Schlemper, G. N. Schrauzer, I. A. Hugues, *Polyhedron* **1984**, *3*, 377−380.
[18] W. A. Herrmann, W. R. Thiel, J. G. Kuchlerf, J. Behm, E. Herdtweck, *Chem. Ber.* **1990**, *123*, 1963−1970.
[19] W. R. Thiel, M. Angstl, T. Preirmeier, *Chem. Ber.* **1994**, *127*, 2373−2379.
[20] W. R. Thiel, T. Preirmeier, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1737−1738.
[21] H. Glass, M. Spiegler, W. R. Thiel, *Eur. J. Inorg. Chem.* **1998**, 275−281.
[22] W. R. Thiel, J. Eppinger, *Chem. Eur. J.* **1997**, *3*, 696−705.
[23] M. Gómez, S. Jansat, G. Muller, D. Panyella, M. Font-Bardía, X. Solans, *J. Chem. Soc., Dalton Trans.* **1997**, 3755−3764.
[24] G. Balavoine, J. C. Clinet, I. Lellouche, *Tetrahedron Lett.* **1989**, *30*, 5141−5144.
[25] J. M. Canal, M. Gómez, F. Jiménez, M. Rocamora, G. Muller, E. Duñach, D. Franco, A. Jiménez, F. H. Cano, *Organometallics* **2000**, *19*, 966−978.
[26] G. M. Sheldrick, SADABS, *A Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany, **1996**, based on the method of Robert Blessing: R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33.
[27] G. M. Sheldrick, SHELXS-97, *A Program for Solving Crystal Structures and Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.

Received April 26, 2004
Early View Article
Published Online August 26, 2004

