Synthesis of methyltrioxorhenium(VII) arylamine complexes and mono- and bis(ortho)-chelated arylaminorhenium(VII) trioxides [1]

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Abstract

From the reaction of $MeReO_3$ with the neutral arylamine $C_6H_5CH_2NMe_2$ and the aryldiamine $C_6H_4(CH_2NMe_2)_2$-1,3, have been isolated in good yields the 1/1 adduct complex $[MeReO_3 \cdot C_6H_5CH_2NMe_2]$, **1**, and the 2/1 adduct complex $[(MeReO_3)_2 \cdot C_6H_4(CH_2NMe_2)_2$-1,3], **2**, respectively. The X-ray molecular structure of **2** shows that both rhenium centres have a trigonal bipyramidal geometry and in the axial positions of each rhenium centre are one of the NMe_2 units of the aryldiamine ligand and a methyl group. The mono(ortho)-chelated arylaminorhenium trioxide complex $[ReO_3\{C_6H_4CH_2NMe_2$-2$\}]$, **3**, can be synthesized by a transmetallation reaction of $ClReO_3$ with $[Zn\{C_6H_4CH_2NMe_2$-2$\}_2]$ in a 2:1 molar ratio. In a similar way the bis(ortho)-chelated arylaminorhenium trioxide complex $[ReO_3\{C_6H_3(CH_2NMe_2)_2$-2,6$\}]$, **4**, can be synthesized by addition of a mixture of $[Li_2\{C_6H_3(CH_2NMe_2)_2$-2,6$\}_2]$ and $ZnCl_2$ to $ClReO_3$. Complexes **3** and **4** have been isolated as white solids in 66% and 81% yields respectively. The rhenium centre in complex **4** has a bicapped tetrahedral geometry in which the monoanionic $\{C_6H_3(CH_2NMe_2)_2$-2,6$\}^-$ ligand is pseudo-facially bonded with a characteristic N1–Re–N2 angle of 107.7(3)°, a $Re-C_{ipso}$ bond length of 2.112(11) Å and Re–N1 and Re–N2 bond lengths of 2.518(9) Å and 2.480(8) Å respectively.

Keywords: Rhenium; Oxide; Arylamine; Crystal structure; Chelate; Bridging ligand

1. Introduction

As a class the organorhenium(VII) oxides $(RReO_3)$ are electron-poor complexes: the metal centre shows a pronounced Lewis acidity, and they readily form adducts with electron-donor ligands such as nitrogen bases [2–4]. One of the most important representatives of this class is methyltrioxorhenium(VII) (MTO), which has been used as a catalyst in various catalytic reactions such as olefin metathesis and epoxidation of alkenes [5]; it has been found that MTO in the presence of an amine base is an excellent catalyst for the latter reaction since it exhibits both high activity and selectivity without a

noticeable induction period [6]. Although MTO is more active in the absence of an amine base, the presence of such a Lewis base is important for suppressing subsequent acid-catalysed ring-opening of the epoxide product [6]. Studies of the solution dynamic behaviour of adduct complexes $RReO_3 \cdot L$ (L = amine donor) have shown that at room temperature the amine coordination to rhenium is labile and that amine dissociation can easily take place, especially in the presence of a donor solvent [7]. As a consequence of this dissociation an open coordination site can be created at the metal centre and in a basic medium OH^- can then coordinate to MTO. The resulting complex $[MeReO_3(OH)]^-$ decomposes readily with formation of methane and perrhenate $[ReO_4]^-$ and this behaviour explains the pronounced water sensitivity of these amine adduct complexes in solution [7]. To make the amine in complexes $[RReO_3 \cdot L]$ less prone to dissociation from the rhenium(VII) centre we are currently investigating the possibility of

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[1] Multiple Bonds Between Main Group Elements and Transition Metals, 160. For Part 159 see Ref. [1].

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synthesizing rhenium complexes which contain potentially intramolecularly coordinating amine ligands. In one of our groups we have recently synthesized two monomeric trioxorhenium complexes, $[ReO_3\{(CH_2)_3NEt_2\}]$ [6] and $[ReO_3\{(CH_2)_3NC_5H_{10}\}]$ [7] in which intramolecular Re–N coordination is operative. Under slightly modified conditions it was also possible to form polymeric $[ReO_3\{(CH_2)_3NEt_2\}]$, which probably contains intermolecular nitrogen–rhenium coordination [6]. Surprisingly, we have found that the monomeric form does not react with H_2O_2 to afford a peroxo complex and that it is inactive in epoxidation chemistry, whereas the polymer, in contrast, is an active catalyst in epoxidation reactions and is more selective than MTO itself [6].

In this paper we now describe the synthesis of two new five-coordinate rhenium species formed by coordination of the neutral tertiary amines N,N'-dimethylbenzylamine $(C_6H_5CH_2NMe_2)$ and α,α'-dimethylamino-1,3-xylene $(C_6H_4(CH_2NMe_2)_2$-1,3), with MTO. The synthesis of two (ortho)-chelated arylaminotrioxorhenium complexes containing the corresponding monoanionic aryl ligands $\{C_6H_4CH_2NMe_2$-2$\}^-$ and $\{C_6H_3(CH_2NMe_2)_2$-2,6$\}^-$ [8] are also reported. These new complexes have been tested as potential catalysts for the epoxidation of cyclohexene.

2. Results and discussion

2.1. Synthesis and characterization of complexes 1 and 2

When a diethyl ether solution of MTO is treated with the monoamine $C_6H_5CH_2NMe_2$ the 1/1 adduct complex $[MeReO_3 \cdot C_6H_5CH_2NMe_2]$, 1, is formed, whereas treatment with the diamine $C_6H_4(CH_2NMe_2)_2$-1,3 affords the 2/1 adduct complex $[(MeReO_3)_2 \cdot C_6H_4(CH_2NMe_2)_2$-1,3], 2 (Scheme 1). Complexes 1 and 2 have been isolated as yellow solids in 78% and 74% yields respectively.

Complex 1 is soluble in both polar and apolar organic solvents like benzene, diethyl ether and pentane. Yellow crystals of 1 can be obtained from a saturated solution in pentane at $-30\,°C$. In contrast, complex 2 is only soluble in polar solvents like dichloromethane or tetrahydrofuran (THF), and it can be obtained as yellow crystals by layering a dichloromethane solution with diethyl ether. Both 1 and 2 are not stable for long periods in air, and to prevent decomposition they are best stored under a nitrogen atmosphere at $-30\,°C$.

Complexes 1 and 2 have been characterized as MTO adduct species with five-coordinate 16-electron Re(VII) metal centres by a variety of techniques, including ^1H and ^{13}C NMR spectroscopy, IR spectroscopy and by an X-ray single crystal diffraction study for 2. The latter
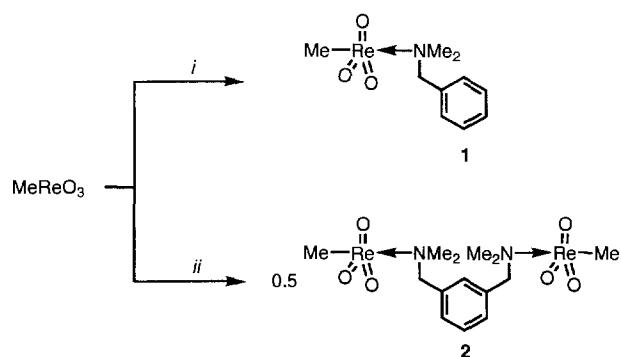
i + $C_6H_5CH_2NMe_2$; Et_2O; RT.

ii + 0.5 $C_6H_4(CH_2NMe_2)_2$-1,3; Et_2O; RT.

Scheme 1. Synthesis of the adduct complexes $[MeReO_3 \cdot C_6H_5CH_2NMe_2]$, 1, and $[(MeReO_3)_2 \cdot C_6H_4(CH_2NMe_2)_2$-1,3], 2.

shows that, in the solid state, complex 2 has two identical $MeReO_3$ units which are bonded, in a bridging fashion, by the two tertiary amine nitrogen donors of the neutral $C_6H_4(CH_2NMe_2)_2$-1,3 aryldiamine ligand (vide infra). Based on the similarity of spectroscopic data (NMR, IR) for 1 and 2 it is proposed, in analogy to 2, that complex 1 has an $MeReO_3$ unit to which the N-donor atom of $C_6H_5CH_2NMe_2$ is bonded.

The IR spectra (KBr) of 1 and 2 both show a $\nu(Re=O)$ at $930\,cm^{-1}$ and these data should be compared with those of the 14-electron complex $MeReO_3$ which has $\nu(Re=O)$ at $965\,cm^{-1}$, and with those of the 16-electron complexes $MeReO_3 \cdot L$ (L = quinuclidine, aniline) which both have a $\nu(Re=O)$ value of $930\,cm^{-1}$ [3]. In the ^1H NMR spectrum (200.13 MHz, $CDCl_3$, 25 °C) of 1 and 2 there is a singlet at 1.75 ppm which can be assigned to the MeRe group; this resonance for MTO ($CDCl_3$) is found at 2.61 ppm. It is known from the literature that the basicity of the coordinated base L in complexes $MeReO_3 \cdot L$ is reflected in the chemical shift value for the MeRe resonance [3]. For example, in the case of the weak base aniline the signal for the Me group is found at 2.54 ppm ($CDCl_3$), whereas for the much stronger base quinuclidine the Me signal is present at 1.40 ppm ($CDCl_3$) [3]. Our ^1H NMR data for 1 and 2 indicate that the tertiary amine donors in these species are coordinated to the MTO unit and that these donors are functioning as strong bases. In the ^{13}C NMR (50.32 MHz, $CDCl_3$, 25 °C) spectrum of 1 and 2 the MeRe signal resonates at 23.6 ppm and 23.5 ppm respectively, whereas the corresponding signal for base-free MTO is found at 19.0 ppm [3].

2.2. Molecular structure of $[(MeReO_3)_2 \cdot C_6H_4(CH_2NMe_2)_2$-1,3] 2

The X-ray molecular structure of 2 is shown in Fig. 1, relevant bond distances and angles are given in Table 1.

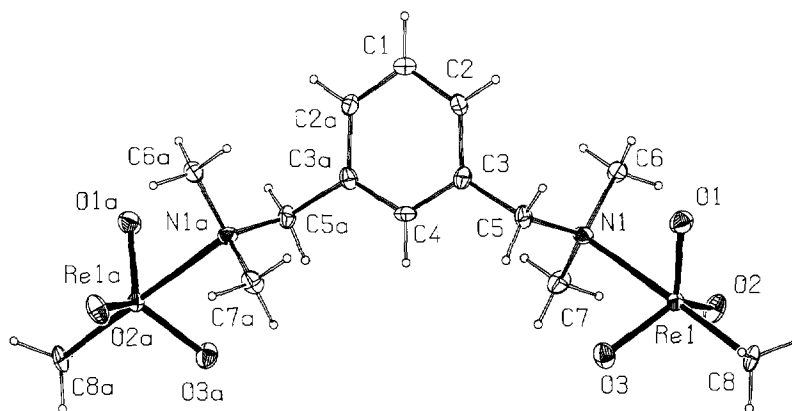Fig. 1. Structure of the 2/1 adduct complex [(MeReO$_3$)$_2$ · C$_6$H$_4$(CH$_2$NMe$_2$)$_2$-1,3], 2; ORTEP drawing with 50% probability ellipsoids.

Fig. 1 shows that 2 contains two MeReO$_3$ units which are each coordinated by one amine nitrogen donor atom of the diamine ligand. This is consistent with an earlier study that showed that MTO can form a 2:1 bridge complex with a diamine ligand which contains two tertiary amine substituents, whereas it forms 1:1 N,N'-chelated complexes with diamine ligands which contain two primary amine substituents [3]. The rhenium centres in the structure of 2 have a trigonal-bipyramidal coordination geometry in which the nitrogen donor and the Me group occupy the axial positions and in which three Re=O bonds define the trigonal plane; the three Re=O bond distances are identical at 1.707(5) Å and the three O–Re–O angles are all close to 118°. This regular planar ReO$_3$ unit in 2 is also a

feature of the molecular structures of the aniline and quinuclidine MTO adduct complexes [MeReO$_3$ · H$_2$NC$_6$H$_5$] and [MeReO$_3$ · N(CH$_2$CH$_2$)$_3$CH] respectively [3,4]. In the X-ray molecular structure of 2 the CH$_2$NMe$_2$ N-donor groups of C$_6$H$_4$(CH$_2$NMe)$_2$-1,3 are positioned on opposite sides of the aryl ring, and in each metal coordination sphere the three N-donor atom substituents (2 × Me, –CH$_2$Ar) are so positioned that they are 'staggered' with regard to the oxygen atoms of the planar ReO$_3$ unit.

2.3. Synthesis of the mono- (3) and bis- (4) (ortho)-chelated arylaminorhenium trioxides

When a THF solution of [Zn{C$_6$H$_4$CH$_2$NMe$_2$-2}$_2$] is added dropwise to a solution of ClReO$_3$ in THF a transmetallation reaction takes place resulting in the formation of [ReO$_3${C$_6$H$_4$CH$_2$NMe$_2$-2}], 3 which has been isolated as a colourless solid in 66% yield (Scheme 2).

Table 1
Selected bond lengths (Å) and bond angles (deg) for 2 and 4

2		4	
Bond lengths			
Re1–O1	1.707(5)	Re1–O1	1.716(7)
Re1–O2	1.707(5)	Re1–O2	1.724(7)
Re1–O3	1.707(5)	Re1–O3	1.730(7)
Re1–N1	2.513(6)	Re1–N1	2.518(9)
Re1–C8	2.097(6)	Re1–N2	2.480(8)
		Re1–C1	2.112(11)
Bond angles			
O1–Re1–O2	118.1(3)	O1–Re1–O2	110.0(4)
O1–Re1–O3	118.2(3)	O1–Re1–N2	169.2(3)
O1–Re1–N1	82.1(2)	O2–Re1–N1	81.1(3)
O1–Re1–C8	98.1(3)	O3–Re1–N1	167.6(3)
O2–Re1–O3	117.9(3)	N1–Re1–N2	107.7(3)
O2–Re1–N1	82.1(2)	O1–Re1–O3	99.8(3)
O2–Re1–C8	98.3(3)	O1–Re1–C1	102.3(4)
O3–Re1–N1	81.6(2)	O2–Re1–N2	80.8(3)
O3–Re1–C8	97.9(3)	O3–Re1–N2	75.9(3)
N1–Re1–C8	179.4(2)	N1–Re1–C1	68.8(3)
Re1–N1–C5	107.8(4)	O1–Re1–N1	74.5(3)
		O2–Re1–O3	111.3(3)
		O2–Re1–C1	127.5(3)
		O3–Re1–C1	102.4(4)
		N2–Re1–C1	69.6(3)
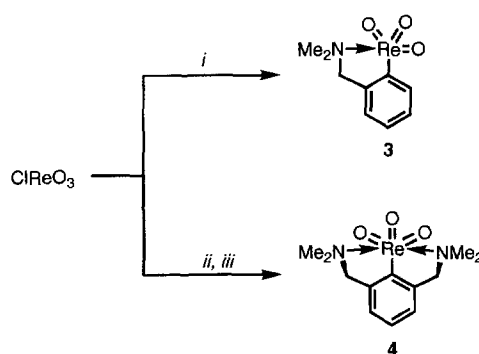
i + 0.5 [Zn{C$_6$H$_4$CH$_2$NMe$_2$-2}$_2$]; - 0.5 ZnCl$_2$; THF; -78 °C.

ii + 0.5 [Li{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}]$_2$ and 0.5 ZnCl$_2$; - 0.5 ZnCl$_2$; - LiCl; THF; -78 °C.

iii + 0.5 [Li{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}]$_2$; - LiCl; THF; -78 °C.

Scheme 2. Synthesis of the σ-bonded arylamine rhenium complexes [ReO$_3${C$_6$H$_4$CH$_2$NMe$_2$-2}], 3, and [ReO$_3${C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}], 4.

The crude product can be crystallized from a saturated solution in a 1:10 toluene–pentane mixture that is cooled to $-30\,^{\circ}$C. Complex **3** is air- and water-stable and is soluble in benzene, toluene and diethyl ether, but is only slightly soluble in apolar solvents like pentane and hexane.

When $ClReO_3$ is reacted with the aryllithium reagent $[Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_2$ a very unclean reaction takes place; from the mixture of products the colourless solid $[ReO_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$, **4**, was isolated in poor yield (4%). However, when $ClReO_3$ is reacted with a reagent mixture prepared from prior addition of $ZnCl_2$ to a THF solution of $[Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_2$ the colour of the reaction mixture turns from light yellow to red-brown and complex **4** can be isolated from this reaction mixture in good yield (81%) (Scheme 2). Complex **4** is soluble in benzene, toluene and diethyl ether but is only slightly soluble in pentane or hexane. Colourless crystals can be obtained on cooling a saturated solution in pentane to $-30\,^{\circ}$C. It is important to note that these syntheses of **3** and **4** afford mononuclear species that possess intramolecular coordination of one or two ortho-chelating CH_2NMe_2 groups respectively, and we found no evidence for polymeric material as a consequence of intermolecular Re–N coordination. This behaviour of chelating arylamine ligands contrasts with that of the anionic alkylamine ligand $\{CH_2CH_2CH_2NEt_3\}^-$. The latter forms what can be considered to be an alkyl analogue of **3**, i.e. $[ReO_3\{(CH_2)_3NEt_2\}]$, and depending on the work-up procedure, this can be obtained either as polymeric or monomeric material in high yield [6]. A possible reason for this difference in behaviour could be the greater rigidity of the aryl carbon backbone connecting the C- and N-donor sites in the ligands in **3** and **4** compared with the corresponding flexible carbon backbone in the γ-alkylamine ligand.

2.4. Molecular structure of $[ReO_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ **4**

The X-ray molecular structure of **4** is shown in Fig. 2 and relevant bond angles and distances are given in Table 1.

The geometry of the 18-electron arylrhenium(VII) complex **4** can be described as a distorted bicapped tetrahedron in which the three oxygen atoms and the σ-bonded aryl carbon atom C(1) form a tetrahedron and the coordination sphere around rhenium is completed by the N-donor atoms N1 and N2 of the CH_2NMe_2 groups. The N,C,N-coordinated $C_6H_3(CH_2NMe_2)_2\text{-}2,6$ ligand hereby adopts a pseudo-facial coordination mode with an Re–Cl bond distance of $2.112(11)\,\text{Å}$ which is similar to that of $2.00(1)\,\text{Å}$ and $2.06(1)\,\text{Å}$ in the aryl trioxorhenium complex $[ReO_3\{C_6H_2Me_3\text{-}1,3,5\}]$ [9], and Re–N bond distances of $2.480(8)\,\text{Å}$ and $2.518(9)\,\text{Å}$ that
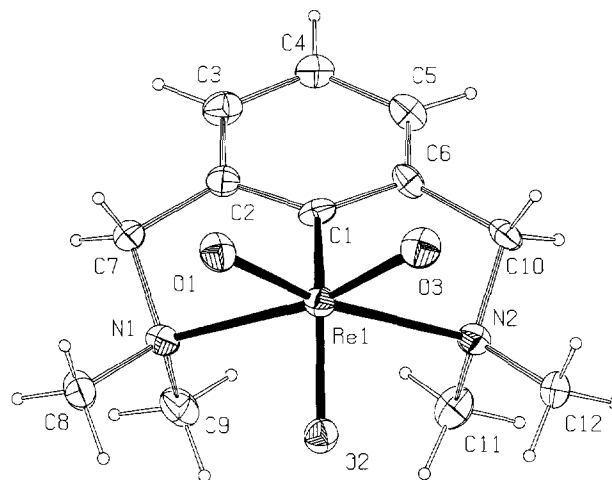
Fig. 2. Structure of the arylaminorhenium complex $[ReO_3\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$, **4**; ORTEP drawing with 50% probability ellipsoids.

are slightly longer than that in the 16-electron complexes $[ReO_3\{(CH_2)_3NEt_2\}]$ $(2.383(3)\,\text{Å})$ and $[ReO_3\{(CH_2)_3N(C_5H_{10})\}]$ $(2.385(4)\,\text{Å})$ [6,7]. The pseudo-facial coordination mode of $C_6H_3(CH_2NMe_2)_2\text{-}2,6$ in **4** is further characterized by an N1-Re-N2 angle of $107.7(3)°$. Other recent examples of fac-N,C,N bonding are $[Ru\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}X(nbd)]$ (nbd = norbornadiene; $X = Cl$, OSO_2CF_3) [10,11] and $[TaCl_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(=CH\text{-}t\text{-}Bu)]$ [11]. The Re–O bond distances of approximately $1.7\,\text{Å}$ are comparable with those in other trioxorhenium complexes described in literature [6,7,12].

2.5. Characterization of complexes 3 and 4 in solution

In the ^1H NMR (200.13 MHz, C_6D_6, 25 $^{\circ}$C) spectrum of mononuclear $[ReO_3\{C_6H_4CH_2NMe_2\text{-}2\}]$, **3**, the NMe_2 and CH_2 resonances, at 2.15 ppm and 3.08 ppm respectively, appear as sharp singlets. This situation can be consistent either with a five-coordinate complex having the N- and C-donor centres located in a molecular symmetry plane or with a four-coordinate complex without Re–N coordination. Since the chemical shift values for the NMe_2 and CH_2 protons of free $C_6H_4CH_2Me_2$ are 2.07 ppm and 3.25 ppm (200.13 MHz, C_6D_6, 25 $^{\circ}$C) respectively, the data for **3** indicate that in solution this species is likely to have coordination of the nitrogen donor of the CH_2NMe_2 group to the metal centre, i.e. **3** probably has a five-coordinate structure. Furthermore, the solid-state structures of the related complexes $[ReO_3\{(CH_2)_3NEt_2\}]$ and $[ReO_3\{(CH_2)_3N(C_5H_{10})\}]$ have shown these species to have five-coordinate trigonal bipyramidal structures in which the nitrogen donor and one oxygen atom occupy the axial positions and the aryl carbon of the C,N coordinating ligands and two oxygen atoms form the equatorial plane [6,7].
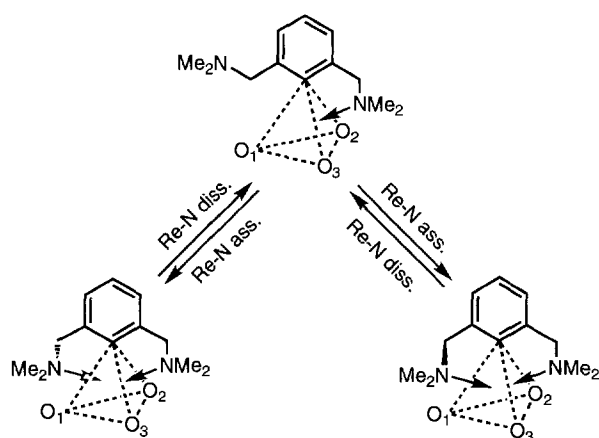
Re is considered to be at the centre of the tetrahedron.

Scheme 3. Postulated fluxional process for 4 in solution.

The ^{1}H NMR spectrum of the bis(ortho)-chelated arylamino complex 4 is strongly temperature dependent and the data are consistent with this species being fluxional in solution. At low temperature (223 K) there are two NMe_2 signals at 1.51 ppm and 2.73 ppm and the CH_2 protons give rise to a well-resolved AB pattern at 2.69 and 3.75 ppm (^2J(H,H) = 13 Hz). These data are in accordance with the solid-state structure of 4 (Fig. 2), i.e. pseudo-facial terdentate N,C,N-coordination of the aryldiamine ligand and the presence of a symmetry plane containing the oxygen atom O2, C_{ipso} and the rhenium centre. In this structure the CH_2NMe_2 substituents are equivalent, though the two Me groups of each NMe_2 unit and the protons of the CH_2 groupings are diastereotopic. Upon raising the temperature of a solution of 4 the CH_2NMe_2 resonances broaden and the CH_2 and NMe_2 groupings eventually become homotopic (CH_2: T_c = 270 K, $\Delta G^\ddagger$ = 51 ± 2 kJ mol^{-1}; NMe_2: T_c = 285 K, $\Delta G^\ddagger$ = 54 ± 2 kJ mol^{-1}). At 298 K the CH_2 unit affords a broad singlet while the methyl resonance for the NMe_2 units is a sharp singlet.

A process which accounts for this fluxional behaviour of 4 is shown in Scheme 3. In the ground-state structure the rhenium centre is considered to be positioned at the centre of a tetrahedral ligand array formed by three O atoms and a σ-bonded C atom with additional coordination of the two nitrogen donors of the CH_2NMe_2 substituents to two triangular O/O/C faces. The first step in the postulated process is Re–N dissociation of one of the coordinated nitrogen donors from the C_{ipso}–O$_1$–O$_2$ face leading to an intermediate in which the aryldiamine ligand is only bonded to the metal by C_{ipso} and one nitrogen donor, i.e. bidentate C,N-coordination. In the second step, face-centred nucleophilic attack of the non-coordinated nitrogen donor on the C_{ipso}–O$_1$–O$_3$ face takes place.

2.6. Reactivity in epoxidation reactions with cyclohexene

The coordination complexes 1 and 2 and the organometallic complexes 3 and 4 have been tested for possible catalytic activity in the epoxidation of cyclohexene by hydrogen peroxide. The complexes 1 and 2 yielded exclusively the epoxide without any detectable formation of the ring-opening product trans-1,2-cyclohexanediol. This activity and selectivity is comparable with that of the Lewis base adduct complexes of MTO described in the literature [6].

The organometallic complexes 3 and 4 do not react with H_2O_2, as monitored by ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C), and do not catalyse olefin epoxidation; after 12 h at 50 °C, neither epoxide nor the acid-catalysed ring-opening product trans-1,2-cyclohexanediol could be detected by GC. This lack of reactivity is in accordance with earlier observations concerning the inactivity of the aryltrioxorhenium complexes, [ReO$_3${C$_6$H$_2$Me$_3$-2,4,6}] and [ReO$_3${C$_6$H$_5$}] in the attempted epoxidation of cyclohexene with hydrogen peroxide [6]. Similarly, the mononuclear C,N-bidentate form of [ReO$_3${(CH$_2$)$_3$NEt$_2$}] was found neither to react with H_2O_2 nor to catalyse olefin epoxidation. However, in this latter study it was found that the polymeric form of [ReO$_3${(CH$_2$)$_3$NEt$_2$}], with intermolecular C,N-coordination, dissolves in aqueous hydrogen peroxide and is active in olefin epoxidation. The reasons for this difference in reactivity between these two different structural forms, as well as the fact that aryltrioxorhenium complexes are inactive, has not yet been explained [6].

3. Conclusions

Through use of C,N-coordinating {C$_6$H$_4$CH$_2$NMe$_2$-2}$^-$ and N,C,N-coordinating {C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}$^-$ we have introduced a new type of chelating ligand to rhenium oxide chemistry. Although the new arylaminorhenium trioxide complexes with intramolecular C,N-coordination are not active as catalysts in the epoxidation of alkenes their easy accessibility and high stability make them excellent starting materials for the synthesis of other aryltrioxorhenium(VII) species.

4. Experimental section

4.1. General

All experiments were performed in a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were stored over sodium benzophenone ketyl and distilled prior to use. Elemental analyses were carried out by Dornis und Kolbe, Microanalytisches Laboratorium,

Mülheim a.d. Ruhr, Germany. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC200 or AC300 spectrometer. IR spectra were recorded on a Mattson FT-IR 5000 spectrometer and GC spectra were recorded on a Philips PU 4600. The compound $(C_6H_4(CH_2NMe_2)_2\text{-}1,3)$ [3] and the complexes $MeReO_3$ [13], $[Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_2$ [14] and $[Zn\{C_6H_4(CH_2NMe_2)\text{-}2\}_2]$ [15] were prepared according to literature procedures. $ClReO_3$ was prepared in situ according to a literature procedure [16]. Both Re_2O_7, obtained from Fluka, and $C_6H_5CH_2NMe_2$, obtained from Acros Organics, were used without further purification.

4.2. [MeReO₃ · C₆H₅CH₂NMe₂], 1

To a solution of $MeReO_3$ (0.52 g, 2.08 mmol) in Et_2O (30 ml) was added a solution of $C_6H_5CH_2NMe_2$ (0.32 g, 2.32 mmol) in Et_2O (10 ml). The resulting solution was stirred for 2 h during which time the colour of the solution gradually changed from colourless to yellow. Et_2O was removed in vacuo and the solid residue was extracted with n-pentane. Large block-shaped yellow crystals of 1 were obtained by cooling a saturated n-pentane solution from +25 to −30 °C; yield 0.62 g (78%). Anal. Found: C, 31.1; H, 4.3; N, 3.7. $C_{10}H_{16}NO_3Re$. Calc.: C, 31.2; H, 4.2; N, 3.6%. ^{1}H NMR (200.13 MHz, CDCl$_3$, 25 °C, TMS): δ 1.75 (s, 3 H, ReMe), 1.99 (s, 6 H, NMe$_2$), 3.41 (s, 2 H, CH$_2$), 7.15 (m, 2 H, ArH), 7.31 (m, 3 H, ArH). ^{13}C NMR (50.32 MHz, CDCl$_3$, 25 °C, TMS): δ 23.6 (ReMe), 43.1 (NMe$_2$), 61.7 (CH$_2$), 128.2 (o-C + p-C), 131.3 (m-C), 132.3 (C$_i$). IR(KBr): ν(Re=O) 930 cm^{-1}.

4.3. [(MeReO₃)₂ · C₆H₅(CH₂NMe₂)₂-1,3], 2

To a solution of $MeReO_3$ (1.36 g, 5.44 mmol) in Et_2O (30 ml) was added a solution of $C_6H_5CH_2NMe_2$-1,3 (0.70 g, 3.73 mmol) in Et_2O (20 ml) and a white precipitate formed. After 30 min the Et_2O solution was decanted off from the precipitate and the crude product was washed with Et_2O (20 ml). Small yellow plate-shaped crystals of 2 were obtained by layering a solution of 2 in CH_2Cl_2 with Et_2O; yield 1.38 g (74%). Anal. Found: C, 24.3; H, 3.7; N, 4.1. $C_{14}H_{26}N_2O_6Re_2$. Calc.: C, 24.3; H, 3.8; N, 4.1%. ^{1}H NMR (200.13 MHz, CDCl$_3$, 25 °C, TMS): δ 1.75 (s, 6 H, ReMe), 1.99 (s, 12 H, NMe$_2$), 3.41 (s, 4 H, CH$_2$), 7.29 (m + s, 2 H, ArH), 7.32 (m, 2 H, ArH). ^{13}C NMR (50.32 MHz, CDCl$_3$, 25 °C, TMS): δ 23.5 (ReMe), 43.2 (NMe$_2$),

61.6 (CH$_2$), 128.0 (C$_i$), 130.9 (m-C), 132.7 (p-C), 134.0 (o-C). IR(KBr): ν(Re=O) 930 cm^{-1}.

4.4. [ReO₃{C₆H₄CH₂NMe₂-2}], 3

To a yellow solution of $ClReO_3$ (0.33 g, 1.24 mmol) in THF (20 ml) was added at −78 °C a colourless solution of $[Zn\{C_6H_4CH_2NMe_2\text{-}2\}_2]$ (0.21 g, 0.62 mmol) in THF (20 ml). The colour of the reaction solution changed from colourless to brown. The solution was stirred at −78 °C for 1 h after which the solution was allowed to warm to room temperature. After 1 h the solvent was removed in vacuo and the remaining brown residue was extracted three times with 25 ml of C_6H_6. The combined extracts were evaporated in vacuo and the white residue was washed with cold n-pentane (10 ml). Colourless needle-shaped crystals were obtained by cooling a saturated toluene–n-pentane solution (1:10) of 3 from +25 to −30 °C; yield 0.45 g (66%). Anal. Found: C, 29.4; H, 3.2; N, 3.9. $C_9H_{12}NO_3Re$. Calc.: C, 29.3; H, 3.3; N, 3.8%. ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C, TMS): δ 2.15 (s, 6 H, NMe$_2$), 3.08 (s, 2 H, CH$_2$), 6.84 (m, 2 H, ArH), 7.08 (m, 1 H, ArH), 8.40 (d, ^3J(H,H) = 8 Hz, 1 H, ArH). ^{13}C NMR (50.32 MHz, C_6D_6, 25 °C, TMS): δ 48.9 (NMe$_2$), 65.5 (CH$_2$), 126.0 (Ar), 128.7 (Ar), 133.0 (Ar), 149.5 (Ar), 151.7 (Ar), 165.1 (ArC$_{ipso}$). IR(KBr): ν(Re=O) 978 (m), 957 (s), 916 (vs) cm^{-1}.

4.5. [ReO₃{C₆H₃(CH₂NMe₂)₂-2,6}], 4 (from ClReO₃ with [Li{C₆H₃(CH₂NMe₂)₂-2,6}]₂ / ZnCl₂)

To a solution of $[Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_2$ (0.29 g, 1.45 mmol) in THF (25 ml) at room temperature was added solid $ZnCl_2$ (0.11 g, 0.80 mmol). The resulting white suspension was added slowly over ca. 2 min to a solution of $ClReO_3$ (0.39 g, 1.45 mmol) in THF (25 ml) at −78 °C. The reaction mixture was allowed to warm over ca. 30 min to room temperature. After 2 h at 25 °C, during which time the colour changed gradually from colourless to brown, the solvent was removed in vacuo and the remaining brown residue was extracted with C_6H_6 (3 × 25 ml). Subsequent in vacuo removal of volatiles from the combined extracts afforded 4 as a white solid. The crude product was recrystallized by cooling a saturated solution of 4 in hexane from +25 to −30 °C; yield 0.50 g (81%) as colourless (very slightly brown) needle-shaped crystals. Anal. Found: C, 33.8; H, 4.6; N, 6.6. $C_{12}H_{19}N_2O_3Re$. Calc.: C, 33.9; H, 4.5; N, 6.6%. ^{1}H NMR (300.13 MHz, C_6D_6, 25 °C, TMS): δ 2.16 (s, 12 H, NMe$_2$), 3.36 (s, 4 H, CH$_2$), 6.84 (d, ^3J(H,H) = 7 Hz, 2 H, ArH), 6.97 (t, ^3J(H,H) = 7 Hz, 1 H, ArH). ^{13}C NMR (50.32 MHz, C_6D_6, 25 °C, TMS): δ 45.4 (NMe$_2$), 66.1 (CH$_2$), 125.5 (Ar), 130.5 (Ar), 152.3 (Ar), 174.8 (ArC$_{ipso}$). IR(KBr): ν(Re=O) 936 (m), 905 (vs) cm^{-1}.

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^{3} $C_6H_4(CH_2NMe_2)_2$-1,3 was prepared from α,α'-diamino-m-xylene by a standard Clark–Eschweiler alkylation procedure. ^{1}H NMR (200.13 MHz, CDCl$_3$, 25 °C): δ 2.27 (s, 12 H, NMe$_2$), 3.45 (s, 4 H, CH$_2$), 7.10–7.35 (m + s, 4 H, ArH).

4.6. $[ReO_3\{C_6H_3(CH_2NMe_2)_2$-$2,6\}]$, 4 (from $ClReO_3$ with $[Li\{C_6H_3(CH_2NMe_2)_2$-$2,6\}]_2$)

A solution of $[Li\{C_6H_3(CH_2NMe_2)_2$-$2,6\}]_2$ (0.23 g, 1.16 mmol) in THF (25 ml) was added to a solution of $ClReO_3$ (0.31 g, 1.16 mmol) in THF (25 ml) at $-78\,^{\circ}C$. The solution was allowed to warm to room temperature over ca. 30 min during which time the colour changed from colourless to brown-black. After 2 h the solvent was removed in vacuo and the remaining brown-black residue was extracted with C_6H_6 (3 × 25 ml). Subsequent removal of C_6H_6 from the combined extracts in vacuo afforded a small amount of 4 as a white solid. The crude product was recrystallized by cooling a saturated solution of 4 in *n*-hexane from $+25$ to $-30\,^{\circ}C$; yield 0.02 g (4%).

4.7. Tests of the catalytic activity of 1–4

The complex (0.02 mmol calc. on Re) was dissolved in 1,4-dioxane (0.5 ml) containing 10% H_2O_2 and to this solution was added 10 mmol (0.82 g) of pure, distilled cyclohexene. The reaction mixture was stirred at room temperature in the case of the coordination complexes 1 and 2 and up to $50\,^{\circ}C$ in the case of the organometallic complexes 3 and 4. Every hour a sample of 100 μl was taken and this was dissolved in 10 ml of Et_2O. The remaining H_2O_2 in these sample solutions was decomposed with a mixture of a catalytic amount of MnO_2 and a stoichiometric amount of anhydrous $MgSO_4$ to remove the resulting water. The resulting suspension was filtered through a glass frit covered with Celite and the filtrate was analysed by GC methods. The product yields were determined by GC (FID detector, DB 17, capillary column, 30 m) with cycloheptanone as an internal standard.

4.8. X-ray structure determination of 2 and 4

Pertinent crystal data, data collection and refinement details are collected in Table 2. X-ray data were collected either on an Enraf–Nonius CAD4T (rotating

Table 2
Crystallographic data for 2 and 4

	2	4
Crystal data		
Formula	$C_{14}H_{26}N_2O_6Re_2$	$C_{12}H_{19}N_2O_3Re$
Mol. wt.	690.78	425.50
Crystal system	orthorhombic	monoclinic
Space group	*Pbcn* (No.60)	$P2_1/c$ (No.14)
a (Å)	5.5869(10)	8.7280(12)
b (Å)	11.631(2)	10.880(3)
c (Å)	29.514(2)	15.637(3)
β (deg)	—	114.579(11)
V (Å³)	1917.9(5)	1350.4(5)
Z	4	4
D_{calc} (g cm⁻³)	2.392	2.093
$F(000)$ (electrons)	1288	816
μ (cm⁻¹)	128.1	90.0
Crystal size (mm³)	0.03 × 0.25 × 0.38	0.03 × 0.30 × 0.55
Data collection		
T (K)	150	100
θ_{min}, θ_{max} (deg)	1.4, 27.5	2.4, 27.5
Wavelength (Å)	Mo Kα (graphite monochromated) 0.71073	Mo Kα (Zr-filtered) 0.71073
Scan type	ω	ω–2θ
$\Delta\omega$ (deg)	$0.80 + 0.35\tan\theta$	$1.25 + 0.35\tan\theta$
Data set	$-7{:}7, -15{:}0, -38{:}38$	$-11{:}11; 0{:}14, -20{:}20$
Total data, unique data, R_{int}	8143, 2185, 0.08	4061, 3114, 0.097
Abs. corr. range (DIFABS)	0.799: 1.686	0.527: 2.178
Refinement		
No. of refined params	113	167
Final R_1 [a]	0.037 (1823 $I_o > 2\sigma(I)$)	0.046 (2435 $I_o > 2\sigma(I)$)
Final wR_2 [b]	0.103	0.124
Goodness of fit	1.09	1.03
Weighting scheme [c]	$1/[\sigma^2(F_o^2) + (0.0597P)^2 + 0.25P]$	$1/[\sigma^2(F_o^2) + (0.0749P)^2 + 8.677P]$
(Δ/σ)max	0.002	0.000
Min./Max. resd. dens. (e Å⁻³)	$-2.02, 1.61$	$-2.99, 2.75$

[a] $R_1 = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [c] $P = (\max(F_o^2, 0.0) + 2F_c^2)/3$.

Table 3

Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for **2**

Atom	x	y	z	U_{eq} (Å^2) [a]
Re1	0.10832(4)	0.18573(2)	0.07069(1)	0.0126(1)
O1	0.2480(11)	0.3142(4)	0.0616(2)	0.0220(16)
O2	−0.1864(9)	0.1741(5)	0.0562(2)	0.0220(16)
O3	0.2130(9)	0.0996(4)	0.1131(2)	0.0210(16)
N1	−0.0646(10)	0.2932(5)	0.1369(2)	0.0140(14)
C1	0	0.5670(9)	0.25	0.022(3)
C2	0.0674(12)	0.5061(6)	0.2121(3)	0.0177(19)
C3	0.0654(11)	0.3865(6)	0.2105(3)	0.0147(17)
C4	0	0.3280(7)	0.25	0.014(3)
C5	0.1359(11)	0.3231(6)	0.1680(3)	0.0153(17)
C6	−0.1882(13)	0.3971(6)	0.1194(3)	0.0187(19)
C7	−0.2369(12)	0.2167(6)	0.1590(3)	0.0180(19)
C8	0.2549(13)	0.0951(6)	0.0159(2)	0.020(2)

[a] U_{eq} is one-third of the trace of the orthogonalized U tensor.

anode) for a yellowish plate-shaped crystal of **2** or on a CAD4F (sealed tube) for a brownish cut-to-size needle-shaped crystal of **4**. Accurate unit-cell parameters were derived from the SET4 [17] setting angles. Data were corrected for Lp, linear decay and absorption (DIFABS) [18]. Both structures were solved by automated Patterson methods (DIRDIF-92) [19]. Refinement on F^2 was carried out by full-matrix least squares techniques (SHELXL-93) [20]. Hydrogen atoms were taken into account at calculated positions and refined riding on their carrier atoms. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with an isotropic thermal parameter related to the value of the equivalent isotropic thermal parame-

Table 4

Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms for **4**

Atom	x	y	z	U_{eq} (Å^2) [a]
Re1	0.22498(4)	0.23244(3)	0.12368(3)	0.0170(1)
O1	0.1458(9)	0.3791(6)	0.1011(5)	0.024(2)
O2	0.0625(8)	0.1274(6)	0.0830(5)	0.0205(19)
O3	0.3191(9)	0.2364(6)	0.2453(5)	0.026(2)
N1	0.1325(10)	0.2634(7)	−0.0503(6)	0.018(2)
N2	0.3917(10)	0.0398(7)	0.1684(6)	0.020(2)
C1	0.4342(11)	0.2432(8)	0.0891(7)	0.018(3)
C2	0.4245(12)	0.3167(9)	0.0144(7)	0.020(3)
C3	0.5713(12)	0.3393(9)	0.0014(7)	0.023(3)
C4	0.7213(12)	0.2847(9)	0.0610(7)	0.023(3)
C5	0.7252(12)	0.1995(9)	0.1275(7)	0.021(3)
C6	0.5818(11)	0.1812(9)	0.1425(6)	0.018(3)
C7	0.2527(12)	0.3583(9)	−0.0524(7)	0.024(3)
C8	−0.0429(12)	0.3129(10)	−0.0954(7)	0.027(3)
C9	0.1400(13)	0.1537(10)	−0.1042(7)	0.027(3)
C10	0.5677(11)	0.0866(9)	0.2105(7)	0.019(3)
C11	0.3648(13)	−0.0436(9)	0.0894(8)	0.026(3)
C12	0.3522(14)	−0.0299(10)	0.2374(7)	0.028(3)

[a] U_{eq} is one-third of the trace of the orthogonalized U tensor.

ter of their carrier atoms by a factor of 1.5 for the methyl hydrogens atoms and 1.2 for other hydrogen atoms (Tables 3 and 4). Neutral scattering factors were taken from the *International Tables for Crystallography* [21]. A final difference map did not show features other than residual absorption artifacts near Re. Geometrical calculations and illustrations were done with PLATON [22]. Complete listings of coordinate, geometrical and reflection data may be obtained from one of the authors (A.L.S.).

Acknowledgements

References

[1] W.A. Herrmann, A.W. Stumpf, T. Priermeier, S. Bogdanovic, V. Dufaud and J.M. Basset, *Angew. Chem.*, in press.

[2] W.A. Herrmann, G. Weichselbaumer and E. Herdtweck, *J. Organomet. Chem., 372* (1989) 371.

[3] W.A. Herrmann, J.G. Kuchler, G. Weichselbaumer, E. Herdtweck and P. Kiprof, *J. Organomet. Chem., 372* (1989) 351.

[4] W.A. Herrmann, F.E. Kühn, C.C. Romão, H.T. Huy, R.W. Fischer, P. Kiprof and W. Scherer, *Chem. Ber., 126* (1993) 45.

[5] (a) W. Adam, W.A. Herrmann, C.R. Saha-Möller and M. Shimizu, *J. Mol. Catal., 97* (1995) 15. (b) W.A. Herrmann, R.W. Fischer, W. Scherer and M.U. Rauch, *Angew. Chem. Int. Ed. Engl., 32* (1993) 1157. (c) P. Huston, J.H. Espenson and A. Bakac, *Inorg. Chem., 32* (1993) 4517. (d) W.A. Herrmann, W. Wagner, U.N. Flessner, U. Volkhardt and H. Komber *Angew. Chem. Int. Ed. Engl., 30* (1991) 1636. (e) W.A. Herrmann and M. Wang, *Angew. Chem. Int. Ed. Engl., 30* (1991) 1641. (f) W.A. Herrmann, R.W. Fischer and D.W. Marz, *Angew. Chem. Int. Ed. Engl., 30* (1991) 1638. (g) S. Yamazaki, J.H. Espenson and P. Huston, *Inorg. Chem., 32* (1993) 4683. (h) Z. Zhu and J.H. Espenson, *J. Mol. Catal., 103* (1995) 87. (i) W. Adam and C.M. Mitchell, *Angew. Chem. Int. Ed. Engl., 35* (1996) 533. (j) W.A. Herrmann *J. Organomet. Chem., 500* (1995) 149.

[6] W.A. Herrmann, R.W. Fischer, M.U. Rauch and W. Scherer., *J. Mol. Catal., 86* (1994) 243.

[7] W.A. Herrmann, F.E. Kühn, M.U. Rauch, J.D.G. Correia and G. Artus, *Inorg. Chem., 34* (1995) 2914.

[8] G. van Koten, *Pure Appl. Chem., 61* (1989) 1681.

[9] (a) W.A. Herrmann, M. Ladwig, P. Kiprof and J. Riede, *J. Organomet. Chem., 371* (1989) C13. (b) C. de Méric de Bellefon, W.A. Herrmann, P. Kiprof and C.R. Whitaker, *Organometallics, 11* (1992) 1072.

[10] J.P. Sutter, S.L. James, P. Steenwinkel, T. Karlen, D.M. Grove, N. Veldman, W.J.J. Smeets, A.L. Spek and G. van Koten, *Organometallics, 15* (1996) 941.

[11] H.C.L. Abbenhuis, N. Feiken, D.M. Grove, J.T.B.H. Jastrzeb-ski, H. Kooijman, P. van der Sluis, W.J.J. Smeets, A.L. Spek and G. van Koten, *J. Am. Chem. Soc., 114* (1992) 9773.

[12] (a) I.A. Degnan, W.A. Herrmann and E. Herdtweck, *Chem. Ber., 123* (1990) 1347. (b) A. Domingos, J. Marçalo, A. Paulo,

A. Pires de Matos and I. Santos, *Inorg. Chem., 32* (1993) 5114. (c) F.E. Kühn, W.A. Herrmann, R. Hahn, M. Elison, J. Blümel and E. Herdtweck, *Organometallics, 13* (1994) 1601. (d) W.A. Herrmann, M. Taillefer, C. de Méric de Bellefon and J. Behm, *Inorg. Chem., 30* (1991) 3247. (e) W.A. Herrmann, P.W. Roesky, F.E. Kühn, M. Elison, G. Artus, W. Scherer, C.C. Romão, A. Opez and J. Basset, *Inorg. Chem., 34* (1995) 4701. (f) A.K. Burrell, F.A. Cotton, L.M. Daniels and V. Petricek, *Inorg. Chem., 34* (1995) 4253.

[13] W.A. Herrmann, F.E. Kühn, R.W. Fischer, W.R. Thiel and C.C. Romão, *Inorg. Chem., 31* (1992) 4431.

[14] J.T.B.H. Jastrzebski, G. van Koten, M. Konijn and C. Stam, *J. Am. Chem. Soc., 104* (1982) 5490.

[15] A. Osman, R.G. Steevenz, D.G. Tuck, H.A. Meinema and J.G. Noltes, *Can. J. Chem., 62* (1984) 1698.

[16] W.A. Herrmann, F.E. Kühn, C.C. Romão, M. Kleine and J. Mink, *Chem. Ber., 127* (1994) 47.

[17] J.L. de Boer and A.J.M. Duisenberg, *Acta Crystallogr. Sect. A:, 40* (1984) C410.

[18] N. Walker and D. Stuart, *Acta Crystallogr. Sect. A:, 39* (1983) 158.

[19] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits and C. Smykalla, *The DIRDIF program system, Tech. Rep.,* 1992 (Crystallography Laboratory, University of Nijmegen, Netherlands).

[20] G.M. Sheldrick, *SHELXL-93 Program for crystal structure refinement,* University of Göttingen, Germany, 1993.

[21] A.J.C. Wilson (ed.), *International Tables for Crystallography,* Vol. C, Kluwer, Dordrecht, 1992.

[22] A.L. Spek, *Acta Crystallogr. Sect. A:, 46* (1990) C34.