

# Ferrocenyl ligands in mixed valence high-oxidation state rhenium complexes

Otto Knoesen<sup>a</sup>, Helmar Görls<sup>b</sup>, Simon Lotz<sup>c,\*</sup>

<sup>a</sup> Atomic Energy Corporation, Pelindaba, Pretoria 0001, South Africa

<sup>b</sup> Department of Chemistry, University of Jena, Jena, Germany

<sup>c</sup> Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa

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Dedicated to Professor Helmut Werner on the occasion of his 65th birthday.

## Abstract

The reactions of the ferrocenyl ligands *dppf* and *dfed* with  $[\text{ReO}(\text{PPh}_3)_2\text{Cl}_3]$  afforded the complexes  $[\text{ReO}(\text{dppf}-P,P')\text{Cl}_3]$  (**1**), which has a *cis-fac* arrangement of ligands, and  $[\text{ReO}_2(\text{dfed}-N,N')_2]^+$  (**3**) (*dppf* = 1,1'-bis(diphenylphosphino)ferrocene and *dfed* = bis(*N,N'*-ferrocenylmethyl)ethylenediamine). In wet ether, **1** converts into  $[\text{ReO}(\text{dppf}-P,P')(\text{OH})\text{Cl}_2]$  (**2**). Crystal structure determinations were performed on **1** and the tetraphenylborate salt of **3**. Compound **1** crystallizes in the orthorhombic system, space group  $P2_12_12_1$  with  $a = 11.5364(2)$ ,  $b = 15.8381(4)$  and  $c = 17.5050(4)$  Å and **3** crystallizes in the orthorhombic system, space group  $Aba2$  with  $a = 15.3773(8)$ ,  $b = 15.1344(7)$  and  $c = 28.2817(14)$  Å. © 2000 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

Numerous examples of complexes with ferrocenyl fragments are being investigated for their potential application in many and diverse areas of Chemistry [1]. Examples of these are: their use in chemical sensors [2], for cation transport across membranes [3], in molecular electronics [4], as agents with anti-tumour properties [5], in dendritic [6] and polymeric materials [7], in materials with non-linear optical properties [8], as liquid crystals [9] and in organic synthesis with the emphasis on processes of asymmetric catalysis [10]. There is considerable interest in the design, synthesis and properties of novel electrochemically active ligands containing redox-active groups such as ferrocenyl in close proximity to other metal centres [11].

The 1,1'-bis(diphenylphosphino)ferrocenyl (*dppf*) ligand is very attractive as a bidentate phosphine ligand because it is available commercially or synthesized eas-

ily, and is the most widely used of this class of reagents [1,12]. Although the ferrocenyl unit has been linked to practically all transition metals in heteronuclear complexes, examples with *dppf* remain in the domain of low oxidation state organometallic compounds [1]. This is also true for mixed Re–Fe complexes which mostly belong to the class Re(I)–carbonyls [13,14]. However, a number of complexes containing the ferrocenyl unit attached to Re(V) via sulfur atoms have been recorded [15]. Binuclear complexes which simultaneously contain reducing iron (Fe(III)) and oxidizing rhenium (Re(I)) metal centers, display optical metal-to-metal charge transfer properties [16]. One electron oxidation processes localized at the ferrocene fragments were observed from cyclic voltammetry measurements for dinuclear ferrocenyl–rhenium(I) complexes [14]. In addition, binuclear Fe(II)–Re(V) complexes also have the potential of finding application in bioinorganic chemistry. Rhenium compounds as therapeutic agents have recently caught the attention of researchers [17] and combined with the anti-tumour properties associated with the ferrocenium ion [5], binuclear complexes of biological importance could become available in the near future.

\* Corresponding author. Tel.: +27-12-4202800; fax: +27-12-3625297.

E-mail address: slotz@nsnperl.up.ac.za (S. Lotz)



Table 1  
Selected spectral data for 1–3

Complex	Ir ( $\nu/\text{cm}^{-1}$ , KBr, $\nu_{\text{Re=O}}$ )	$^1\text{H}$ - and $^{13}\text{C}$ -NMR ( $\delta/\text{ppm}$ in acetone- $d^6$ )
<b>1</b>	999(vs)	$^1\text{H}$ -NMR. Cp: 4.70 (CH <sub>2</sub> ,5), 4.42 (CH <sub>3</sub> ,4)
	969(vs)	Ph: 7.72 (t, <i>o</i> ), 7.40 (t, <i>p</i> ), 7.35 (m, <i>m</i> ) $^{13}\text{C}$ -NMR. Cp: 80.1( <i>i</i> ), 76.7(C2–5), 75.3(C2,5), 73.1(C3,4) Ph: 134.8( <i>o</i> ), 130.7( <i>p</i> ), 127.3( <i>m</i> ) $^{31}\text{P}$ -NMR. 20.7
<b>2</b> <sup>a</sup>	968(vs)	$^1\text{H}$ -NMR. Cp: 5.29 (CH <sub>2</sub> ,5), 4.45 (CH <sub>3</sub> ,4)
	909(vs)	Ph: 7.90 (t, <i>o</i> ), 7.42 (t, <i>p</i> ), 7.35 (m, <i>m</i> ). OH: 0.04 (s) $^{13}\text{C}$ -NMR. Cp: 80.9( <i>i</i> ), 77.0(C2–5), 76.2(C2,5), 73.6(C3,4) Ph: 135.1( <i>o</i> ), 131.3( <i>p</i> ), 128.4( <i>m</i> ) $^{31}\text{P}$ -NMR. 26.4
<b>3</b>	810	$^1\text{H}$ -NMR. Cp: 4.14(C1–5), 4.20, 4.18(C2,5), 4.26(C3,4) Ph(BPh <sub>4</sub> <sup>−</sup> ): 7.34(br, <i>o</i> ), 6.93(t, <i>m</i> ), 6.78(s, <i>p</i> ) Other: 3.96, 3.92(s, FcCH <sub>2</sub> ), 3.61, 3.51(t, NCH <sub>2</sub> ), 3.10, 2.92(br, NH) $^{13}\text{C}$ -NMR. Cp: 81.9( <i>i</i> ), 69.4(C2–5), 73.3(C2,5), 71.2(C3,4) Ph(BPh <sub>4</sub> <sup>−</sup> ): 165.0–164.0( <i>i</i> ), 137.0( <i>o</i> ), 125.9( <i>m</i> ), 122.2( <i>p</i> ) Other: 61.9, 54.7 (FcCH <sub>2</sub> ), 50.8, 49.4 (NCH <sub>2</sub> )

<sup>a</sup> NMR spectra measured in CDCl<sub>3</sub>.

Cl<sub>3</sub>] with two equivalents *dfed* in refluxing ethanol afforded the dioxo complex **3**. The new complexes were characterized using a combination of infrared,  $^1\text{H}$ -,  $^{13}\text{C}$ - and  $^{31}\text{P}$ -NMR spectroscopy, and mass spectrometry, X-ray crystallography, and elemental analysis. The scheme also includes two intermediate complexes even though no evidence for their presence during the formation of either **2** or **3** was found in the reaction mixture. These are incorporated to clarify conversions and because they form part of a general reaction pathway for the synthesis of complexes containing the Re=O and O=Re=O units. The first intermediate is included to explain the conversion of **1** into **2**. Water is introduced into the mixture coincidentally during recrystallization from dichloromethane and wet ether mixtures. A pure sample of **2** could only be obtained after several recrystallizations from the solvent mixture or by stirring **1** in wet solvents such as acetone or THF (Table 1).

The infrared spectrum of **2**, recorded as a KBr pellet, display strong  $\nu_{\text{Re=O}}$  modes of 968 and 909  $\text{cm}^{-1}$  which is at a lower frequency than the corresponding Re=O vibration frequencies of 999 and 969  $\text{cm}^{-1}$  observed for **1**. The latter compares well with similar vibration frequencies of Re(V) complexes with chloro ligands *trans*

to oxo ligands such as 992 and 980  $\text{cm}^{-1}$  recorded for the analogous *cis*–*fac*-isomers [ReOCl<sub>3</sub>(PMe<sub>3</sub>)<sub>2</sub>] [29] and [ReOCl<sub>3</sub>(*diphos*-*P,P'*)] [32], respectively. The Re=O stretching mode for oxo-hydroxo and oxo-alkoxo complexes is expected in the range 940–975  $\text{cm}^{-1}$  [30]. The chemical shift in the  $^1\text{H}$ -NMR spectrum of **2** for the coordinated OH ligand was observed at 0.04 ppm.

As far as we are aware, complexes of Re(V) containing phosphine ligands and the *trans* oxo-aqua arrangement (first intermediate) have not yet been isolated. The coordination of the bidentate *dppf* ligand requires the scrambling of a *trans* chloro ligand to a *cis* position to facilitate the formation of **1**. The chloro ligand *trans* to the oxo ligand is labilized under these circumstances and readily displaced by other oxygen donor ligands. Complexes of the type [ReO(OEt)(PR<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] are often formed when reactions are performed in wet ethanol [30]. The bonding properties between the softer phosphorous donor atoms and the harder Re(V) center inhibit any further chloro substitutions in the equatorial plane by a second *dppf* ligand.

Refluxing [ReO(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>] with excess *dfed* resulted in the reaction mixture changing from a green suspension to an orange solution from which **3** was isolated. The positive charge on the Re(V) center is better neutralized by a *dfed* ligand compared to a *dppf* ligand and further substitutions of chloro ligands by a second *dfed* ligand are achieved. Complex **3** displays a single O=Re=O asymmetrical stretching mode at 810  $\text{cm}^{-1}$ , consistent with a *trans*-dioxo geometry and within the range of 810–825  $\text{cm}^{-1}$  accepted for aliphatic amine ligands [25b,33]. This value is the same as the corresponding vibration in [ReO<sub>2</sub>(*en*)<sub>2</sub>][ReO<sub>4</sub>] [34] and represents a higher wave number than the value of 788  $\text{cm}^{-1}$  recorded for [ReO<sub>2</sub>(*cyclam*)]<sup>+</sup> [35]. The chemical shifts of the protons in the  $^1\text{H}$ -NMR spectrum of **3** are shifted significantly downfield compared to the corresponding resonances of the free *dfed* ligand [18,20] on complexation to the O=Re=O core. Furthermore, the protons associated with the atoms in the chelate ring, the methylene protons of the ferrocenyl substituent and the cyclopentadienyl protons of the substituted ferrocenyl ring are diastereotopic as a result of the complexation of the nitrogen atoms to the Re-center, the conformations of the chelate rings and the anisotropy of the Re=O bonds. Assignments were supported by 2D HETCOR experiments in CDCl<sub>3</sub> and protons from the  $^1\text{H}$ -NMR spectrum were correlated with carbon resonances from the  $^{13}\text{C}$ -NMR spectrum. The FcCH<sub>2</sub> proton multiplets at 4.34 and 4.31 ppm (partly obscured by the Cp signal at 4.30 ppm) correlate with the carbon resonance at 57.1 ppm, the NCH<sub>2</sub> resonances at 4.25 and 4.24 ppm correlate with a resonance at 56.1 ppm, the unsubstituted Cp rings display a strong singlet at 4.22 ppm which correlates with a resonance at 69.6 ppm, the substituted Cp ring display singlets at 4.63,

4.60, 4.47 and 4.36 ppm correlating with 71.4, 71.4, 71.9 and 72.0 ppm, respectively. The NH resonates as two broad signals at 3.94 and 3.98 ppm and the *ipso*-carbon (Cp) at 85.6 ppm (Fig. 1).

Under the prevailing reaction conditions the formation of an aqua complex will be unfavorable and a direct substitution of the *trans* chloro ligand by a hydroxo ligand, analogous to **2**, is envisaged. The formation of a cationic oxo-aqua complex,  $[\text{ReO}(\text{OH}_2)(\text{cyclam})]^+$ , in aqueous solution has been recorded before by Parker and Roy [36]. Examples of complexes displaying *trans* oxo-hydroxo ligands have been fully characterized [23,37] and Lock and co-workers succeeded in isolating *trans*- $[\text{ReO}(\text{OEt})(\text{py})_2\text{Cl}_2]$  [38]. The complex *trans*- $[\text{ReO}(\text{OEt})(\text{cyclam})]^{2+}$  is known [35], and *trans*- $[\text{ReO}(\text{OMe})(\text{amine})_4]^{2+}$  was prepared by the methylation of the corresponding dioxo complexes [39,40]. The presence of an excess of pyridine invariably leads to the formation of *trans*- $[\text{ReO}_2(\text{py})_4]^+$  [41].

Not observed during the reactions leading to the formation of **3** or **2**, but nevertheless important in this

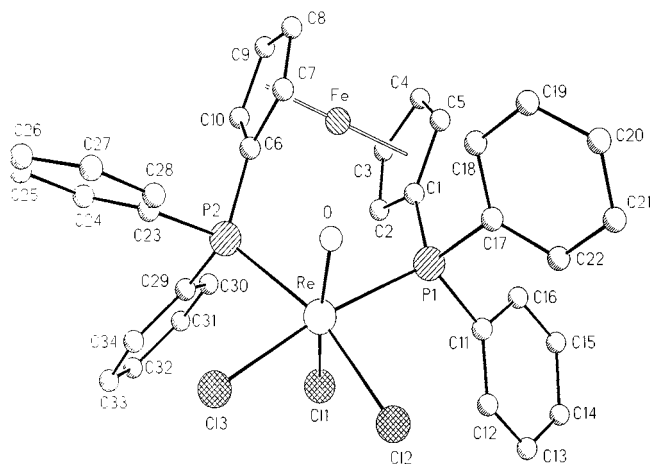


Fig. 1. The molecular structure of  $[\text{ReO}(\text{dppf-P,P}')\text{Cl}_3]$  (**1**) in the solid state showing the atom labeling scheme.

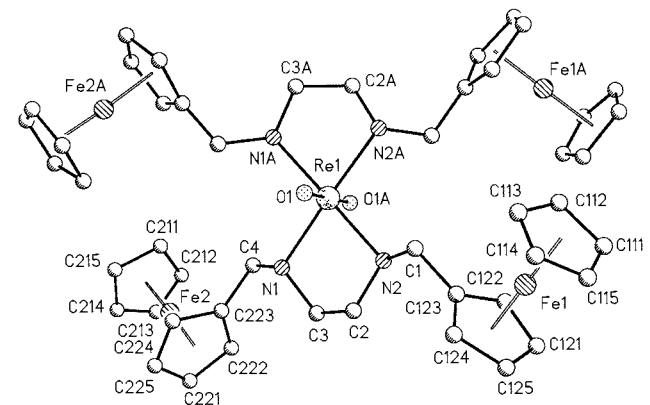


Fig. 2. The molecular structure of  $[\text{ReO}_2(\text{dfed-N,N}')_2]^+$  (**3**) in the solid state showing the atom labeling scheme.

context, is the formation of  $\mu$ -oxo dinuclear complexes [42–44]. These are readily formed from rhenium(V) complexes with alkoxo or hydroxo groups *trans* to the oxo ligand. A water elimination reaction between two hydroxo complexes affording the oxygen bridged dinuclear species has been proposed and accepted and we think represents an alternative route to the direct deprotonation of a hydroxo intermediate affording the  $\text{O}=\text{Re}=\text{O}$  unit. Factors determining the formation and stabilization of  $\mu$ -oxo dinuclear complexes as well as the conversion of the dinuclear complex to the mononuclear dioxo complex have not yet been investigated systematically and are dependent on reaction conditions. Interestingly,  $[(\mu\text{-O})\{\text{ReO}(\text{py})_2\text{Cl}_2\}_2]$  displayed *cis-cis* arrangements of ligands in the equatorial planes of the  $\text{O}=\text{Re}-\text{O}-\text{Re}=\text{O}$  axis [45]. Although the possibility of an oxygen bridged dinuclear complex as unstable intermediate during the reaction with *dfed* to give **3** can not be excluded, it is a less likely route, as the presence of basic *dfed* could directly deprotonate the hydroxo species to afford the  $\text{O}=\text{Re}=\text{O}$  core. This route is further supported by the formation of  $[\text{dfedH}]^+$  during the reaction. The presence of  $[\text{dfedH}]\text{Cl}$  in the reaction mixture complicated the purification of **3**, but was circumvented by using sodium acetate as an auxiliary base.

The stepwise transformation of the  $\text{Re}=\text{O}$  to the  $\text{O}=\text{Re}=\text{O}$  core by the deprotonation of a water ligand and subsequent deprotonation of the resulting hydroxo ligand or the reverse processes of protonation of an oxo ligand from the  $\text{O}=\text{Re}=\text{O}$  precursor, have previously been suggested [34,37,46]. In conclusion, the neutralization of the high charge on the metal, structural constraints of the chelating ligand employed, the pH of the reaction medium and the reaction conditions drive the reaction to the mono-oxo or dioxo products. The more basic reaction medium and under harsher reaction conditions such is the case during the reaction with *dfed* instead of *dppf*, the reaction proceeds to a final product which contains two oxo ligands,  $[\text{ReO}_2(\text{dfed})_2]^+$  (**3**). Also, for the chelating ligand, the harder nitrogen donor atoms associate more favourable with the harder  $\text{Re(V)}$  center than the softer P-atoms. Whether the substitution process by a second *dfed* ligand precedes the deprotonation of a hydroxo ligand is not clear at this moment and requires further kinetic investigations (Fig. 2).

In spite of the fact that (i) technetium and rhenium dioxo complexes have been characterized with 1,3-diaminopropane ligands [47]; (ii) the analogous bis-ferrocenyl ligand *dfpd* is known [19]; and (iii) we observed similar changes in color of the reaction mixture during the reaction for the *dfed*- and *dfpd*-ligands, a pure sample of  $[\text{ReO}_2(\text{dfpd})_2]^+$  could not be isolated for characterization.

Table 2  
Selected bond lengths (Å) and bond angles (°) for **1**

Bond lengths			
Re–O	1.755(8)	Re–Cl(3)	2.360(3)
Re–Cl(1)	2.371(3)	Re–Cl(2)	2.395(3)
Re–P(2)	2.503(3)	Re–P(1)	2.508(3)
Fe–C(6)	2.027(11)	Fe–C(ringA) <sup>a</sup>	2.059(13)
Fe–C(ringB) <sup>a</sup>	2.060(13)	P(1)–C(1)	1.802(11)
P(1)–C(17)	1.842(11)	P(1)–C(11)	1.847(13)
P(2)–C(6)	1.802(12)	P(2)–C(29)	1.823(11)
P(2)–C(23)	1.849(12)	C–C(ringA) <sup>a</sup>	1.43(2)
C–C(ringB) <sup>a</sup>	1.43(2)		
Bond angles			
O–Re–Cl(3)	102.7(3)	O–Re–Cl(1)	164.1(2)
Cl(3)–Re–Cl(1)	91.1(1)	O–Re–Cl(2)	98.7(2)
Cl(3)–Re–Cl(2)	85.3(1)	Cl(1)–Re–Cl(2)	90.2(1)
O–Re–P(2)	88.9(2)	Cl(3)–Re–P(2)	80.8(1)
Cl(1)–Re–P(2)	85.5(1)	O–Re–P(1)	85.4(2)
P(2)–Re–P(1)	102.9(1)	C(1)–P(1)–Re	117.0(4)
C(17)–P(1)–Re	108.7(4)	C(11)–P(1)–Re	118.3(4)
C(6)–P(2)–Re	117.0(4)	C(29)–P(2)–Re	113.6(4)
C(23)–P(2)–Re	111.3(4)		

<sup>a</sup> Averaged values for distances of Cp rings.

Table 3  
Selected bond lengths (Å) and angles (°) for **3**<sup>a</sup>

Bond lengths			
Re(1)–O(1)	1.774(8)	Re(1)–N(1)	2.190(13)
Re(1)–N(2)	2.218(12)	Fe–C(ringA) <sup>b</sup>	2.04(2)
N(1)–C(3)	1.49(2)	N(1)–C(4)2	1.51(2)
C(1)–N(2)	1.50(2)	C(1)–C(123)	1.52(2)
Fe–C(ringA) <sup>b</sup>	2.02(2)	N(2)–C(2)	1.48(2)
C(2)–C(3)	1.50(2)	C(4)–C(223)	1.51(2)
C–C(ringA) <sup>b</sup>	1.37(6)	C–C(ringB) <sup>b</sup>	1.45(4)
C–C(ringA) <sup>b</sup>	1.42(5)	C–C(ringB) <sup>b</sup>	1.43(6)
Bond angles			
O(1) # 1–Re(1)–O(1)	179.8(1)	O(1) # 1–Re(1)–N(1)	87.6(5)
O(1)–Re(1)–N(1)	92.4(5)	N(1)–Re(1)–N(1) # 1	101.7(7)
O(1) # 1–Re(1)–N(2)	92.2(5)	O(1)–Re(1)–N(2)	87.7(5)
N(1)–Re(1)–N(2)	79.2(4)	N(1) # 1–Re(1)–N(2)	175.3(5)
N(2)–Re(1)–N(2) # 1	100.3(6)	C(2)–N(2)–C(1)	109.7(11)
C(2)–N(2)–Re(1)	108.6(8)	C(1)–N(2)–Re(1)	114.1(8)
N(2)–C(2)–C(3)	107.8(12)	N(1)–C(3)–C(2)	110.1(13)
C(223)–C(4)–N(1) # 4	113.4(11)		

<sup>a</sup> Mirror image bond lengths are not repeated in the table.

<sup>b</sup> Averaged values are given; ring A represent the substituted and ring B the unsubstituted Cp-rings. Symmetry transformations used to generate equivalent atoms: # 1  $-x, -y+1, z$ ; # 2  $-x, -y+1/2, z+1/2$ ; # 3  $-x, -y+2, z$ ; # 4  $-x, -y+1/2, z-1/2$ .

## 2.2. Structural studies

The molecular structures of [ReO(*dppf*-*P,P'*)Cl<sub>3</sub>] (**1**) and [ReO<sub>2</sub>(*dfed*)<sub>2</sub>]<sup>+</sup> (**3**) were confirmed by single crystal X-ray diffraction studies. Selected bond distances and angles are given in Tables 2 and 3, while Figs. 1 and 2 show the molecular structures and the atomic numbering schemes used for **1** and **3**[BPh<sub>4</sub>]·2H<sub>2</sub>O, respectively.

In **1**, the rhenium atom is found in a distorted octahedral environment with the phosphorous atoms of the *dppf* ligand *trans* to chloro ligands in the rare *cis-fac* configuration. Crystals studied by X-ray diffraction which have the same configuration of ligands are [ReO(*diphos*)X<sub>3</sub>] (X = Cl, Br) [48] and [ReO-(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>] [29]. The cyclopentadienyl rings of the *dppf* ligand are planar within experimental error, but deviate slightly from being parallel by inclining towards each other at the rhenium side of the dinuclear complex; the angle between the two Cp least-squares planes is 2.7°. Although the spacing between the rings decreases towards the phosphine substituents, the phosphorous atoms bend outwards due to their coordination to the rhenium. The P-atoms are 0.161 and 0.079 Å above the planes of the cyclopentadienyl rings for P1 and P2, respectively. The two cyclopentadienyl rings are in a gauched conformation with a torsion angle of 39.1°. The torsion angle is defined by C1–X1–X2–C6 (X1 and X2 are the centroids of the Cp rings). The coordination of the *dppf* ligand, the ring tilt, the displacement of the P atom and the conformation of the two cyclopentadienyl rings cause the octahedral environment at the Re center to be severely distorted. As a result, the P1–Re–P2 angle increases from 90 to 102.9(1)°, which consequently affects the rest of the structure. This is seen in the equatorial plane in the angles P1–Re–Cl2 and P2–Re–Cl3, which are 171.2(1) and 165.4(1)°, respectively, as well as in the positions of the two axial atoms O and Cl1. These two atoms are displaced away from the space occupied by the bulky *dppf* ligand, affording a O–Re–Cl1 angle of 164.1(2)°. The P1–Re–P2 angle, as well as the bonding properties of the ligands are probably the most important reasons for inhibiting the substitution of the two ancillary ligands in the equatorial plane by a second *dppf* ligand. Even though bite angles of 97–104° (P–M–P') have been found in square planar complexes [49], these angles are generally smaller in octahedral complexes and values of 95.3 and 93.6° have been recorded for [Mo(*dppf*-*P,P'*)(CO)<sub>4</sub>] [50] and *fac*-[Re(*dppf*-*P,P'*)(CO)<sub>3</sub>Cl] [14], respectively. Although synthesized and characterized spectroscopically some years ago [30], the crystal structure of [ReO(*diphos*)Cl<sub>3</sub>] was only determined much later [48]. The corresponding bite angles of 83.3(3) and 81.20(4)° for the *diphos* ligands in [ReO(*diphos*)Cl<sub>3</sub>] and [TcO(OH)<sub>2</sub>(*dmpe*)<sub>2</sub>]<sup>2+</sup> [51] are representative of these angles in chelates of this type. These values are significantly smaller than the value of 102.7° recorded for **1**. Unfortunately structural data of the starting compound [ReO(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>] could only be obtained for one of the three possible stereoisomers, i.e. the *mer-trans* isomer, which rules out any meaningful comparisons [52]. However, a very similar bond angle of 102.9(1)° was recorded for the *cis-fac* isomer

of [ReO(PMe<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>] [29], which indicates that the electronic properties of the oxo rather than steric features of the *dppf* ligand are responsible for the large distortions in the octahedral geometry of the complex. See Table 2.

The nonbonding distance of 4.408(6) Å between Re and Fe falls between the corresponding distances of 4.506 Å in [Re(*dppf*-*P,P'*)(CO)<sub>3</sub>Cl] [14] and 4.389 Å in the ferrocenyl carbon disulfide complex, [ReOTp)-(S<sub>2</sub>Fc')] (Fc' = ferrocendyl, Tp = hydrido-*tris*(1-pyrazolyl)borate) [15b]. The corresponding Mn...Fe distance for the lighter manganese in [Mn(MeCp)(*dppf*-*P,P'*)(CO)] is 4.308(2) Å [53]. The Re–O bond length of 1.755(8) Å is long for Re(V)=O distances as comparable distances for similar complexes fall in the range 1.67–1.71 Å [29,52]. However, a similar distance of 1.76(1) Å was recorded for [ReO(OEt)(PPh<sub>3</sub>)<sub>2</sub>-Cl<sub>2</sub>] [48]. The Re–P bond lengths of 2.503(3) and 2.508(3) of **1** are significantly longer than the average Re–P distance of 2.445(2) Å for [ReO(*diphos*)Cl<sub>3</sub>] [48].

The molecular structure of [ReO<sub>2</sub>(*dfed*-*N,N'*)<sub>2</sub>]BPh<sub>4</sub> consists of **3** and the BPh<sub>4</sub><sup>-</sup> anion and two water crystallization molecules. A mirror plane exists in the complex, both in the cationic and anionic molecules, resulting in that only half of the molecule could be determined while the other half is duplicated on the mirror plane. Complex **3** reveals a six-coordinated geometry for the rhenium atom with the two oxide ligands *trans* in the axial positions and the two ferrocenyl-containing bidentate *dfed*-*N,N'* ligands in the equatorial plane to make up the cation. The four nitrogen atoms of the basal plane are planar and the rhenium atom lies in this plane. The small bond angle around Re, N(1)–Re–N(2), in the five-membered ring (79.2(4)°) is again due to the geometrical constraints in coordinated ethylenediamine-type ligands and compare with similar angles of 80.0(3), 83.0(3) and 84.6(2)° for [ReO<sub>2</sub>(*en*)<sub>2</sub>]<sup>+</sup> [34,54], ReO<sub>2</sub>(*cyclam*)<sup>+</sup> [35] and [CuO<sub>2</sub>(*dfed*-*N,N'*)<sub>2</sub>]<sup>+</sup> [20], respectively. To compensate, angles of 101.7(7) and 100.3(6)° were recorded for neighboring *dfed*-ligands N(1)–Re–N(1A) and N(2)–Re–N(2A), respectively. Contrary to **1**, the above distortions did not prevent the coordination of a second *dfed*-ligand in the equatorial plane of **3**, which displays two *dfed*-ligands. The five-membered Re–N(1)–C(3)–C(2)–N(2) rings adopt λ-conformations and no important distortions are present in the ferrocenyl moieties which all display eclipsed conformations for the cyclopentadienyl rings. The O=Re=O group is linear (179.9(1)°) and the Re=O distance of 1.744(8) Å compares well with distances of 1.769(1) and 1.761 Å for [ReO<sub>2</sub>(*en*)<sub>2</sub>]<sup>+</sup> [54], 1.775(9) Å for [ReO<sub>2</sub>(*cyclam*)]<sup>+</sup> [35] and 1.765(3) Å for [ReO<sub>2</sub>(2-*MeImH*)<sub>4</sub>]<sup>+</sup> [46b] (Table 3).

### 3. Experimental

#### 3.1. General details

Reactions were carried out in laboratories equipped with inert facilities and solvents were dried when required by usual procedures and distilled before use. Starting materials were purchased from commercial sources and used as received. These include ferrocene-carboxaldehyde, *dppf* and ethylene- and 1,3-propylenediamine. The ferrocenyl ligands *dfed* and *dfpd* (*dfpd* = bis{*N,N'*-ferrocenylmethylpropylenediamine}) were synthesized according to literature procedures [18,19] and the precursor *trans*-[ReO(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>3</sub>] was prepared from the commercially available potassium perrhenate by the method of Chatt [30].

NMR spectra were recorded with a Bruker AC-300 spectrometer with reference to the deuterium signal of the solvent employed. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were measured at 300.15 and 75.469 MHz, respectively. IR spectra were recorded as KBr discs on a Galaxy 3000 FT spectrophotometer and mass spectra on a Finnegan 8200 instrument operating at 70 eV. Elemental analyses were performed by the Analytical Division (PMCT) of the Council for Scientific and Industrial Research, Pretoria.

#### 3.2. Synthesis

##### 3.2.1. Preparation of 1,1'-bis(diphenylphosphino)-ferrocenyl(trichloro)oxorhenium(V) (**1**)

[ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] (417 mg; 0.5 mmol) and *dppf* (1.25 g; 2.25 mmol) were refluxed in dry THF (60 cm<sup>3</sup>) for 30 min. The color of the suspension turned green–brown. The solvent was reduced to 15 cm<sup>3</sup> and the resultant precipitate filtered and washed with THF and air-dried. The light-brown precipitate, turning green upon dissolution in dichloromethane, was filtered and layered with diethyl ether. The resultant dark green plates were filtered, washed with diethylether and air-dried. The yield of **1** was 155 mg (36%, 0.36 mmol).

**1**. Anal. Calc. For C<sub>34</sub>H<sub>28</sub>P<sub>2</sub>Cl<sub>3</sub>OFeRe: C, 47.32; H, 3.27. Found: C, 47.33; H, 3.22%.

MS (EI, *m/z*): 863 (M<sup>+</sup>), 616 (Re<sub>2</sub>O<sub>2</sub>Cl<sub>6</sub><sup>+</sup>), 554 (*dppf*<sup>+</sup>), 308 (ReOCl<sub>3</sub><sup>+</sup>), 292 (ReCl<sub>3</sub><sup>+</sup>), 202 (ReO<sup>+</sup>).

IR (KBr, cm<sup>-1</sup>): 3090, 1484, 1087, 830 (Fc); 999(Re=O).

##### 3.2.2. Preparation of 1,1'-bis(diphenylphosphino)-ferrocenyl(dichloro)(hydroxo)oxorhenium(V) (**2**)

Treatment of 100 mg of **1** with aqueous acetone or THF or repetitive recrystallization from wet ether resulted in the formation of [ReO(*dppf*-*P,P'*)(OH)Cl<sub>2</sub>] (**2**). The solvent was removed under reduced pressure,

the residue redissolved in ether and **2** crystallized from an ether–dichloromethane mixture to give 62 mg (0.07 mmol, 64%) of **2**.

**2**. Anal. Calc. For  $C_{34}H_{29}P_2Cl_2O_2FeRe$ : C, 48.35; H, 3.46. Found: C, 48.25; H, 3.34%.

MS (EI,  $m/z$ ): 845 ( $M^+$ ). IR (KBr,  $cm^{-1}$ ): 3090, 1484, 1087, 830 (Fc); 966 (Re=O).

### 3.2.3. Preparation of bis(*N,N'*-ferrocenylmethyl)-ethylenediaminedioxorhenium(*V*)tetraphenylborate (**3**)

$[ReOCl_3(PPh_3)_2]$  (83 mg; 0.1 mmol), *dfed* (109 mg; 0.24 mmol) and  $NaO(O)CCH_3$  (35 mg) were refluxed in ethanol (15  $cm^3$ ) for 40 min. The orange solution was cooled, filtered and the white precipitate washed with ethanol (5  $cm^3$ ).  $NaBPh_4$  (68 mg; 0.2 mmol) in ethanol (2  $cm^3$ ) was added and the solution left at room temperature for 24 h. The orange crystals that formed were filtered, washed with ethanol and recrystallized from the slow evaporation of a dichloromethane–ethanol solution giving yellow flakes. The slow evaporation of an acetonitrile–water solution yielded orange blocks. The yield of **3** was 64 mg (44%).

**3**. Anal. Calc. For  $C_{72}H_{76}N_4O_2Fe_2ReB$ : C, 59.64; H, 5.28; N, 3.86. Found: C, 59.44; H, 5.19; N, 3.76%. IR (KBr,  $cm^{-1}$ ): 3260 (br, NH) 3100, 1465, 1115, 1010 (Fc); 810 (O=Re=O).

$^1H$ -NMR ( $CDCl_3$ ,  $\delta$ , ppm): 4.34, 4.31 (FcCH<sub>2</sub>), 4.25, 4.24 (NCH<sub>2</sub>), 3.94, 3.98 (NH) 4.22 (Cp:CH 1–5), 4.36, 4.47, 4.60, 4.63 (Cp:CH<sub>2</sub>, 3, 4, 5), 6.67 (Ph: *p*), 6.69 (Ph: *m*), 7.33 (Ph: *o*).

$^{13}C$ -NMR ( $CDCl_3$ ,  $\delta$ , ppm): 57.1 (FcCH<sub>2</sub>), 56.1 (NCH<sub>2</sub>), 69.6 (Cp: C1–5), 85.6, 72.0, 71.4 (Cp: C1; C2,5; C3,4), 163.1, 122.2, 125.9, 137.1 (Ph: *ipso*, *p*, *m*, *o*).

### 3.2.4. Reaction of *dfpd* and $[ReOCl_3(PPh_3)_2]$

This reaction was performed similar to the preparation of **3** but using *dfpd* instead. Again the reaction proceeded as was the case with *dfed* and the solution changed orange, but the reaction mixture consisted of a mixture of products which could not be purified as before.

## 3.3. Crystal structure determination

The intensity data for the compound **1** were collected on a Nonius KappaCCD, while the data of compound **3** were collected on a 1K SMART Siemens CCD area detector diffractometer, using graphite-monochromated Mo– $K_{\alpha}$  radiation. Data were corrected for Lorentz and polarization effects, but not for absorption [55,56]. The structures were solved by direct methods (SHELXS [57]) and refined by full-matrix least-squares techniques against  $F_o^2$  (SHELXL-97 [58]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray

Instruments, Inc.) was used for structure representations.

Crystal Data for **1**:  $C_{34}H_{28}Cl_3FeOP_2Re$ ,  $M_r = 862.90$  g mol<sup>-1</sup>, dark green prism, size 0.38 × 0.32 × 0.28 mm<sup>3</sup>, orthorhombic, space group  $P2_12_12_1$ ,  $a = 11.5364(2)$ ,  $b = 15.8381(4)$ ,  $c = 17.5050(4)$  Å,  $V = 3198.4(1)$  Å<sup>3</sup>,  $T = -90^\circ C$ ,  $Z = 4$ ,  $\rho_{calc.} = 1.792$  g cm<sup>-3</sup>,  $\mu$  (Mo– $K_{\alpha}$ ) = 46.13 cm<sup>-1</sup>,  $F(000) = 1688$ , 8574 reflections in  $h(0/12)$ ,  $k(-17/17)$ ,  $l(-19/19)$ , measured in the range  $3.12 \leq \Theta \leq 23.29^\circ$ , completeness  $\Theta_{max} = 99.5\%$ , 4600 independent reflections,  $R_{int} = 0.055$ , 4508 reflections with  $F_o > 4\sigma(F_o)$ , 381 parameters, 0 restraints,  $R1_{obs} = 0.049$ ,  $wR_{obs}^2 = 0.129$ ,  $R1_{all} = 0.0505$ ,  $wR_{all}^2 = 0.1309$ , Goodness-of-fit = 1.021, Flack-parameter 0.55(1), largest difference peak and hole: 1.659/–1.900 e Å<sup>-3</sup>.

Crystal Data for **3**:  $C_{72}H_{72}BF_4N_4O_6Re$ ,  $M_r = 1509.75$  g mol<sup>-1</sup>, orange–brown prism, size 0.10 × 0.07 × 0.07 mm<sup>3</sup>, orthorhombic, space group  $Aba2$ ,  $a = 15.3773(8)$ ,  $b = 15.1344(7)$ ,  $c = 28.282(1)$  Å,  $V = 6581.9(6)$  Å<sup>3</sup>,  $T = -90^\circ C$ ,  $Z = 4$ ,  $\rho_{calc.} = 1.524$  g cm<sup>-3</sup>,  $\mu$  (Mo– $K_{\alpha}$ ) = 27.48 cm<sup>-1</sup>,  $F(000) = 3056$ , 19277 reflections in  $h(-19/19)$ ,  $k(-20/11)$ ,  $l(-31/36)$ , measured in the range  $1.44 \leq \Theta \leq 28.30^\circ$ , completeness  $\Theta_{max} = 99.5\%$ , 6358 independent reflections,  $R_{int} = 0.091$ , 4508 reflections with  $F_o > 4\sigma(F_o)$ , 398 parameters, 1 restraints,  $R1_{obs} = 0.082$ ,  $wR_{obs}^2 = 0.173$ ,  $R1_{all} = 0.127$ ,  $wR_{all}^2 = 0.197$ , Goodness-of-fit = 1.134, Flack-parameter 0.02(2), largest difference peak and hole: 1.852/0.938 e Å<sup>-3</sup>.

## 4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 119755 for compound **1** and CCDC no. 119756 for compound **3**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44-1223-336033, or e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk].

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