Inorg. Chem. **2001,** *40,* 1199−1205

Structures of a Tetradentate Ferrocenyl Ligand and Its Oxorhenium(V) Complex in Solution and in the Solid State

Otto Knoesen,[†] Philippus L. Wessels,[‡] Helmar Görls,[§] and Simon Lotz*,[‡]

South African Nuclear Energy Corporation, P.O. Box 582, Pretoria 0001, South Africa, Department of Chemistry, University of Pretoria, Pretoria 0002, South Africa, and Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität Jena, Lessingstrasse 8, 07743 Jena, Germany

Received July 7, 2000

The novel ferrocenyl ligand *rac*-1,6-diferrocenyl-*N*,*N*′-bis(2-hydroxypropyl)-2,5-diazahexane (**1**, H_2L) was synthesized from ferrocenylcarboxaldehyde and ethylenediamine followed by the reduction of the Schiff base with $LiAlH_4$ and subsequent N-alkylation with 1,2-propyleneoxide. The dianion of H_2L reacted with $[ReO(PPh_3)_2Cl_3]$, and the product was treated with NH_4PF_6 to afford the complex $[ReO(L\text{-}N_2O_2)PPh_3]PF_6$ (**2**). Both the ferrocenyl ligand and the complex were characterized in solution by NMR spectroscopy and in the solid state by single-crystal X-ray diffraction studies. NMR investigations reveal two solvent-dependent isomers for the ferrocenyl ligand in solution of which the major form is the more ordered one. The cation of **2** displays a nonsymmetrically coordinated N_2O_2 ligand.

Introduction

Since the discovery of ferrocene 50 years ago,[1] the subsequent structure elucidation thereof,[2] and the resulting renaissance in organometallic chemistry,[3] ferrocenyl chemistry has remained on the forefront of new developments in chemistry.[4] Currently a new branch of chemistry is developing around the incorporation of ferrocenyl units into complex molecules containing transition metals. This area is commonly referred to as the chemistry of ferrocenyl ligands[4] whereby the characteristic qualities of ferrocene are introduced into the larger complex. Ferrocenylcarboxaldehyde[5] is a convenient precursor for Schiff base chemistry and has been used to synthesize ferrocenyl and bisferrocenyl derivatives with imine and amine functionalities.[6] As far as we are aware, no examples of ferrocenyl ligands containing tetradentate N_2O_2-donor atoms have been documented in the literature.

Sal_2en-type ligands are well-known tetradentate Schiff bases and provide a rigid, planar,[7] or an unsymmetrical nonplanar N_2O_2-coordination environment for the metal.[8] In the former arrangement both the imine nitrogen donor atoms are trans to the oxygen donor atoms in the complex,[9] whereas the latter represents two pairs of enantiomers displaying only one trans N−O pair. These nonsymmetrically orientated N_2O_2 ligands have three of the four donor atoms in the equatorial plane of the molecule. The final two enantiomers display an arrangement of one trans O−O pair perpendicular to two N-donor atoms in the equatorial plane of the complex.[9] Diverse applications are found for many examples ranging from early to late transition metal complexes containing salen derivatives as ligands. These include the asymmetric catalytic properties of chiral metallosalen complexes in epoxidation[10] and cyclopropanation[11] reactions of olefins, catalytic properties in sulfide oxidations[12] and in promotion of Diels−Alder reactions,[13] and myocardial imaging[14] properties of technetium(III)−salen type complexes.

---

* To whom correspondence should be addressed. E-mail: slotz@nsnper1.up.ac.za.

[†] South African Nuclear Energy Corporation.

[‡] University of Pretoria.

[§] Friedrich-Schiller-Universität Jena.

(1) (a) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039−1040. (b) Miller, S. A.; Tebboth, J. A.; Tremaine, J. F. *J. Chem. Soc.* **1952**, 632−634.

(2) (a) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125−2126. (b) Fischer, E. O.; Pfab, W. *Z. Naturforsch., B* **1952**, *7*, 377−379.

(3) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982. *Comprehensive Organometallic Chemistry II*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1995.

(4) General review. *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995.

(5) (a) Bublitz, D. E.; Rhinehart, K. L. *Org. React.* **1969**, *17*, 1. (b) Graham, P. J.; Lindsey, R. V.; Parshall, G. W.; Peterson, M. L.; Whitman, G. M. *J. Am. Chem. Soc.* **1957**, *79*, 3416−3420.

(6) (a) Neuse, E. W.; Meirim, M. G.; Blom, N. F. *Organometallics* **1988**, *7*, 2562−2565. (b) Benito, A.; Cano, J.; Martínez-Máñez, R.; Soto, I.; Payá, J.; Lloret, F.; Julve, M.; Faus, J.; Marcos, M. D. *Inorg. Chem.* **1993**, *32*, 1197−1203. (c) Kim, E.-J.; Kwon, S.-G.; Shim, S.-G.; Kim, T.-J.; Jeong, J. H. *Bull. Korean Chem. Soc.* **1997**, *18*, 579−582. (d) Song, J.-H.; Cho, D.-J.; Jeon, S.-J.; Kim, Y.-H.; Kim, T.-J.; Jeong, J. H. *Inorg. Chem.* **1999**, *38*, 893−896.

(7) Calligaris, M.; Randaccio, L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, 1987; Vol. 2, Chapter 20.

(8) (a) Chen, H.; White, P. S.; Gagné, M. R. *Organometallics* **1998**, *17*, 5358−5366. (b) Jurisson, S.; Lindoy, L. F.; Dancey, K. P.; McPartlin, M.; Tasker, P. A.; Uppal, D. K.; Deutsch, E. *Inorg. Chem.* **1984**, *23*, 227−231. (c) Sharghi, H.; Naemi, H. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1523−1531. (d) Miyasaki, H.; Ieda, H.; Matsumoto, N.; Re, N.; Crescenzi, R.; Floriani, C. *Inorg. Chem.* **1998**, *37*, 255−163. (e) Kuchta, M.-C.; Hahn, J. M.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **1999**, 3559−3563.

(9) Herrmann, W. A.; Rauch, M. U.; Artus, G. R. J. *Inorg. Chem.* **1996**, *35*, 1988−1991.

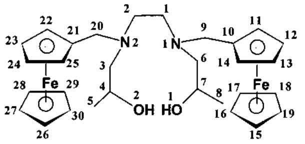
(10) (a) Jogensen, A. K. *Chem. Rev.* **1989**, *89*, 189−214. (b) Pospisil, P. J.; Carsten, D. H.; Jacobsen, E. N. *Chem.—Eur. J.* **1996**, *2*, 974−980. (c) Takeda, T.; Irie, R.; Shinoda, Y.; Katsuki, T. *Synlett* **1999**, 1157−1159.

(11) (a) Fakuda, T.; Katsuki, L. *Tetrahedron* **1997**, *53*, 7201−7208. (b) Uchida, T.; Irie, R.; Katsuki, T. *Synlett* **1999**, 1163−1165.

(12) (a) Bolm, C.; Bienewald, F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2640−2642. (b) Fakuda, T.; Katsuki, L. *Tetrahedron Lett.* **1997**, *38*, 3435−3438.

(13) (a) Schaus, S. E.; Brånalt, J.; Jacobsen, E. N. *J. Org. Chem.* **1998**, *63*, 403−405. (b) Mihara, J.; Hamada, T.; Takeda, T.; Irie, R.; Katsuki, T. *Synlett* **1999**, 1160−1162.

10.1021/ic000746y CCC: $20.00



1

Figure 1. Atom numbering for *N*,*N*′-bis(ferrocenylmethyl)-4,7-diazadecane-2,9-diol.

This paper describes the synthesis and characterization of a novel ferrocenyl *N₂O₂*-tetradentate ligand *rac*-1,6-diferrocenyl-*N*,*N*′-bis(2-hydroxypropyl)-2,5-diazahexane (Figure 1), generated via Schiff base methodology, and the resulting cationic rhenium(V) complex obtained from the reaction with [ReO(PPh$_3$)$_2$Cl$_3$].[15] Both are crystalline materials and well soluble in organic solvents, and the rhenium complex displays a nonsymmetrically orientated N_2O_2 ligand. The results also include a complete NMR analysis in solution as well as single-crystal structure determinations to compare the molecular structure of ligand and complex in solution with those in the solid state.

The first Schiff base complex of rhenium was reported in 1979 by Wilkinson and co-workers.[16] Similar to the above-mentioned N_2O_2-tetradentate Schiff base ligands, the corresponding ferrocenyl ligand in octahedral oxorhenium(V) complexes described in this paper can theoretically adopt any of four different configurations, totaling seven stereoisomers of which three pairs exist as enantiomers.[9] Structures where the ligands lie in the equatorial plane with respect to the Re═O bond dominate in the literature.[7,17] However, the geometry of Schiff base ligands has often in the past been assigned incorrectly because of insufficient or misinterpreted spectral data.

Experimental Section

All common laboratory chemicals used were of reagent grade. Ferrocenylcarboxaldehyde was prepared according to the literature procedure,[5] and 1,6-diferrocenyl-2,5-diazahexane was prepared by slight modification of the procedure of Benito and co-workers.[6b] The precursor [ReO(PPh$_3$)$_2$Cl$_3$] was synthesized according to the method described by Wilkinson and co-workers.[18] Triphenylphosphine and 1,2-propyleneoxide were used as obtained without further purification. Elemental analyses were done at the Council for Scientific Research, Pretoria. Infrared spectra were recorded as KBr disks on a Bomem Michelson 100 FTIR spectrophotometer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained in deuterated chloroform on a Bruker AMXR500 (^{1}H, 500.13 MHz; ^{13}C, 125.72 MHz; ^{31}P, 202.40 MHz) spectrometer. ^{1}H and ^{13}C chemical shifts are relative to SiMe$_4$ measured for ^{1}H from internal CHCl$_3$ ($\delta_H = 7.240$) and for ^{13}C from internal CDCl$_3$ ($\delta_C = 77.00$). ^{31}P chemical shifts are relative to external phosphoric acid ($\delta_P = 0.00$). Standard Bruker microprograms were used for performing the 2D experiments. In the ROESY experiment a mixing time of 250 ms was used.

1,6-Diferrocenyl-*N*,*N*′-bis(2-hydroxypropyl)-2,5-diazahexane (1, H$_2$L). 1. Ferrocenylcarboxaldehyde. Ferrocenylcarboxaldehyde[5] was prepared from ferrocene, and the composition of the product was confirmed spectroscopically. ^{1}H NMR (CDCl$_3$, δ in ppm): 4.33 (s, 5H, C$_5$H$_5$); 4.76 (d, 4H, C$_5$H$_4$); 10.02 (s, 1H, CHO).

2. 1,6-Diferrocenyl-2,5-diazahexa-1,5-diene. 1,6-Diferrocenyl-2,5-diazahexa-1,5-diene[6] was prepared from ferrocenylcarboxaldehyde and characterized with NMR spectroscopy. ^{1}H NMR (CDCl$_3$, δ in ppm): 3.75 (s, 4H, CH$_2$CH$_2$); 4.14 (s, 10H, 2 × C$_5$H$_5$); 4.30 (t, 4H, 4 × Cp); 4.60 (t, 4H, 4 × Cp); 8.14 (s, 2H, 2 × CH).

3. 1,6-Diferrocenyl-2,5-diazahexane. 1,6-Diferrocenyl-2,5-diazahexa-1,5-diene (9.5 g, 0.021 mol) was reduced with LiAlH$_4$ (1.75 g, 0.046 mol added in several portions) in diethyl ether (400 cm^3) under an argon atmosphere and was stirred at room temperature for 24 h. The excess LiAlH$_4$ was hydrolyzed and treated by the successive additions of water (1.7 cm^3), NaOH (15%, 1.7 cm^3), and water (5.1 cm^3). After filtration, the solvent was removed and the product recrystallized from CH$_2$Cl$_2$/heptane. A yield of 8.43 g (88%) was obtained.

Anal. Calcd (%) for C$_{24}$H$_{28}$N$_2$Fe$_2$: C, 63.19; H, 6.19; N, 6.14. Found (%): C, 63.03; H, 6.12; N, 6.16.

4. 1,6-Diferrocenyl-*N*,*N*′-bis(2-hydroxypropyl)-2,5-diazahexane (1, H$_2$L). A solution of 1,6-diferrocenyl-2,5-diazahexane (2.28 g, 0.005 mol) and 1,2-propyleneoxide (0.64 g, 0.011 mol) was stirred in absolute ethanol (20 cm^3) at ambient temperature for 4 days. The yellow precipitate was filtered and washed with cold ethanol. The yield was 1.61 g (56%). The filtrate was evaporated to dryness, dissolved in CH$_2$Cl$_2$, and loaded onto a silica gel column prepared in CH$_2$Cl$_2$. A second fraction of the product was obtained by eluting with methanol ($R_f = 0.5$). Yield: 1.21 g (41%). The combined yield of **1** obtained was 97%. Anal. Calcd (%) for C$_{30}$H$_{40}$N$_2$O$_2$Fe$_2$: C, 62.95; H, 7.04; N, 4.89. Found (%): C, 62.91; H, 7.02; N, 4.94. MS (*m*/*z*): 572 (M$^+$), 554 (M$^+$ − H$_2$O), 373 (M$^+$ − FcCH$_2$), 355 (M$^+$ − FcCH$_2$−H$_2$O), 286 ($^1/_2$M$^+$), 199 (FcCH$_2$$^+$), 186 (Fc$^+$). IR (KBr, ν (cm^{-1})): 3080, 1455, 1105, 1005, 825 (ferrocenyl); 1030 (C−O).

(*N*,*N*′-Bis(ferrocenylmethyl)-4,7-diazadecane-2,9-dioxo-*N₂O₂*)-triphenylphosphineoxorhenium(V) Hexafluorophosphate (2). [ReO(PPh$_3$)$_2$Cl$_3$] (83 mg, 0.1 mmol), H$_2$L (**1**, 68 mg, 0.11 mmol), and NaOC(O)CH$_3$ (40 mg) were refluxed in ethanol (20 cm^3) for 30 min. The volume was reduced to 5 cm^3, and diethyl ether (60 cm^3) was added. A white precipitate (NaCl) was filtered off after 10 min. A solution of NH$_4$PF$_6$ (32 mg, 0.22 mmol) in ethanol (2 cm^3) was added to the filtrate, and the solution evaporated to dryness. The solid was extracted with CH$_2$Cl$_2$, dried with Na$_2$SO$_4$ (gravity filtration), filtered, and layered with hexane. The green crystals were filtered, washed with hexane, and dried. Yield of **2** was 49 mg (39%). Anal. Calcd (%) for C$_{48}$H$_{53}$N$_2$O$_3$P$_2$F$_6$Fe$_2$Re: C, 48.86; H, 4.53; N, 2.38. Found (%): C, 48.30; H, 4.89; N, 2.25. MS (*m*/*z*): [M$^+$] was not observed. Principal ion [L-N_2O_2]$^+$ = 572. IR (KBr, ν (cm^{-1})): 3100, 1463, 1106, 999, 825 (ferrocenyl); 917 (Re═O); 1020 (C−O); 1437 (PPh$_3$); 837 (PF$_6$).

Crystal Structure Determination of H$_2$L and [ReO(L-*N₂O₂*)PPh$_3$]-PF$_6$. Single crystals of **1** and **2**, suitable for X-ray crystallography, were grown by the slow evaporation of a CH$_2$Cl$_2$/hexane mixture. The intensity data were collected on a NONIUS KappaCCD area detector diffractometer, using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects but not for absorption.[19,20] The structures were solved by direct methods (SHELXS[21]) and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97[22]). The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. Complex **1** crystallized in two symmetry-independent molecules **A** and **B**. Both molecules show a disordered hydroxyl group

---

(14) De Rosch, M. A.; Brodack, J. W.; Grummon, G. D.; Marmion, M.; Nosco, D. L.; Deutsch, K. F.; Deutsch, E. *J. Nucl. Med.* **1992**, *33*, 850−854.

(15) Part of the work was reported at a conference, and an abstract was subsequently published in the conference proceedings. Knoesen, O.; Lotz, S. In *Technetium, Rhenium and other Metals in Chemistry and Nuclear Medicine*; Nicolini, M., Mazzi, U., Eds.; SGE Editoriali: Padova, Italy, 1999; pp 153−156.

(16) Middleton, A. R.; Masters, A. F.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1979**, 542−545.

(17) (a) Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Dolmella, A. *Inorg. Chim. Acta* **1989**, *164*, 127−135. (b) Marchi, A.; Duatti, A.; Rossi, R.; Magon, L.; Mazzi, U.; Pasquetto, A. *Inorg. Chim. Acta* **1984**, *81*, 15−19.

(18) Johnson, N. P.; Lock, C. J. L.; Wilkinson, G. *J. Chem. Soc.* **1964**, 1054−1056.

(19) *COLLECT, Data Collection Software*; Nonius B.V.: Delft, The Netherlands, 1998.

(20) Otwinowski, Z.; Minor, W. Processing of X-Ray Diffraction Data Collected in Oscillation Mode. In *Macromolecular Crystallography, Part A*; Carter, C. W., Sweet, R. M., Eds.; *Methods in Enzymology 276*; Academic Press: San Diego, CA, 1997; pp 307−326.

(21) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

(22) Sheldrick, G. M. *SHELXL-97*, release 97-2; University of Göttigen: Göttigen, Germany, 1997.

Scheme 1

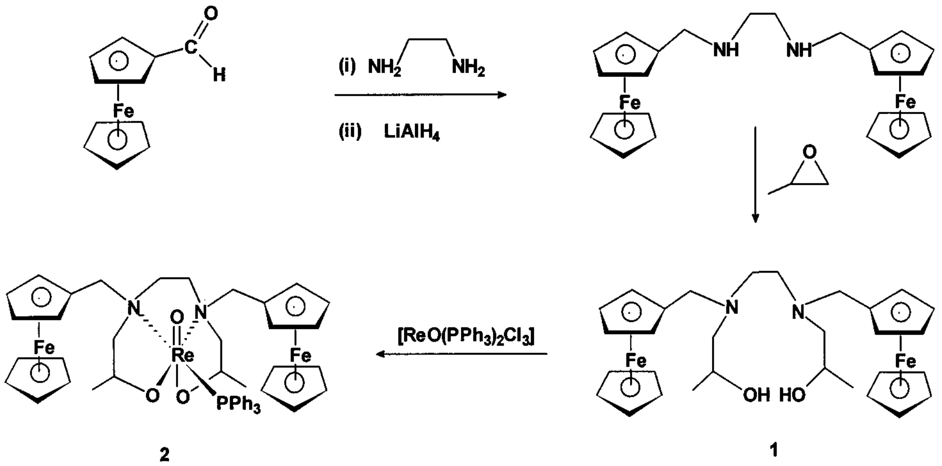


Table 1. Crystal Data for H_2L (**1**) and $[ReO(L)PPh_3]PF_6$ (**2**)

	1	**2**
chemical formula	$C_{30}H_{40}Fe_2N_2O_2$	$C_{48}H_{53}F_6Fe_2N_2O_3P_2Re$
fw	572.34	1179.76
temp (°C)	−90(2)	20(2)
λ (Mo Kα) (Å)	0.71073	0.71073
space group	$P2_1/c$	$R3c$
a (Å)	18.616(3)	28.7628(3)
b (Å)	10.551(2)	28.7628(3)
c (Å)	28.274(4)	33.2935(7)
α (deg)	90	90
β (deg)	98.34(1)	90
γ (deg)	90	120
vol (Å^3)	5494.8(16)	23853.5(6)
Z	8	8
D(calc) (g/cm^3)	1.384	1.478
final R indices[a] [$I > 2\sigma(I)$]	R1 = 0.0492, wR2 = 0.0974	R1 = 0.0349, wR2 = 0.0929
R indices[a] (all data)	R1 = 0.1468, wR2 = 0.1290	R1 = 0.0394, R2 = 0.1081

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where P is $[2F_c^2 + \max(F_o^2,0)]/3$. GOF $= \{\sum[(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

O1. The disorder could be solved. Compound **2** is twinned, and the refinements were based on TWIN and BASF instructions. XP (Siemens Analytical X-ray Instruments, Inc.) was used for structure representations. Crystal data are summarized in Table 1.

Results and Discussion

The ferrocenyl ligand 1,6-diferrocenyl-2,5-diazahexane was synthesized by the condensation of 2 equiv of ferrocenylcarboxaldehyde with 1,2-ethylenediamine to afford the Schiff base bisimine intermediate.[6] The latter was isolated and reduced by lithium aluminum hydride in diethyl ether to produce the diamine in good yields. In recent literature reports the hydrogenation was either carried out catalytically with $[Rh(COD)(dppf)]ClO_4$ or stoichiometrically with $KHFe(CO)_4$.[6c] Final purification was achieved by forming the *p*-toluenesulfonate salt in acetone. The ferrocenyl ligand was regenerated as a yellow-brown powder by neutralizing an aqueous solution of ligand with sodium bicarbonate. Spectral data were in good agreement with literature reports for the identical compound.[6] Ferrocenyl-substituted ethylenediimine and -diamine ligands have been used in the coordination chemistry of rhenium[23] and other transition metals.[6a,b] The ligand 1,6-diferrocenyl-*N*,*N*′-bis(2-hydroxypropyl)-2,5-diazahexane (**1**, H_2L) was synthesized by the N,N′-dialkylation of 1,6-diferrocenyl-2,5-diazahexane with 1,2-propyleneoxide in ethanol and represents a racemic mixture of isomers. Analytically pure **1** precipitated as a yellow powder. The rhenium complex $[ReO(L\text{-}O,N,N,O)PPh_3]PF_6$ (**2**) was isolated from the reaction of $[ReO(PPh_3)_2Cl_3]$ with **1** in refluxing ethanol and in the presence of NH_4PF_6 and sodium acetate as a proton sponge. Complex **2** is stable in polar solvents. Scheme 1 presents the syntheses of **1** and **2** and Figure 1 the atom labeling used for the NMR spectroscopy.

The spectral data of **2** are consistent with the solid-state structure determination and confirm an octahedral ligand environment around the rhenium metal. The N_2O_2 ligand is nonsymmetrical with an oxygen donor atom trans to Re═O. Whereas the reaction of $[ReO(PPh_3)_2Cl_3]$ with bis(trimethylsilyl)-*N*,*N*′-ethylenebis(salicylideneiminato) gave a dinuclear complex in which the sal$_2$en ligand bidentately bridges two $ReO(PPh_3)Cl_2$ fragments,[24] the same rhenium precursor, with bis(salicylideneimine) ligands containing three and four carbons in the alkyl chains that bridge the imino groups, yielded neutral alkoxy complexes with symmetrical and nonsymmetrical N_2O_2 ligands.[25] The results revealed that the configuration of the N_2O_2 ligands in the complexes was dependent on the length of the alkyl chain and the boiling point of the alcohol used for the reactions. Even though the same reaction conditions were used in the present synthesis, complex **2** is unique because a phosphine ligand had been retained, resulting in a cationic Re(V) complex with a nonsymmetrical N_2O_2 ligand. Other differences between the above-mentioned complexes and **2** are the ferrocenyl substituents, the amine nitrogen donor atoms affording more flexible rings, and the shorter chain length of the carbon spacer unit. Symmetrical sal$_2$en complexes with alkoxy ligands react with water to give oxygen-bridged dirhenium complexes containing a O═Re−O−Re═O backbone.[25] Similar complexes were isolated for N_2O_2 ligands with amine nitrogen donor atoms from $[ReOCl_4]^-$ and $[ReOCl_5]^{2-}$ precursors.[26,27]

Whereas the infrared spectra of **1** and **2** reveal all the characteristic bands of the ferrocenyl moiety, this is not true

---

(23) Knoesen, O.; Görls, H.; Lotz, S. *J. Organomet. Chem.* **2000**, *598*, 108−115.

(24) Bombieri, G.; Mazzi, U.; Gilli, G.; Hermandez-Cano, F. *J. Organomet. Chem.* **1978**, *159*, 53−62.

(25) Van Bommel, K. J. C.; Verboom, W.; Kooijman, H.; Spek, A. L.; Reinhoudt, D. N. *Inorg. Chem.* **1998**, *37*, 4197−4203.

(26) Pillai, M. R. A.; Barnes, C. L.; Schlemper, E. O. *Polyhedron* **1994**, *13*, 701−708.

(27) Abram, U.; Abram, S.; Mäcke, H. R.; Koch, P. *Z. Anorg. Allg. Chem.* **1995**, *621*, 854−860.

Table 2. ^{1}H and ^{13}C NMR Data[a] (**1**)

	major isomer			minor isomer		
proton/carbon	δ_H[b] (ppm)	$J(HH)$[c] (Hz)	δ_C (ppm)	δ_H[b] (ppm)	$J(HH)$[c] (Hz)	δ_C (ppm)
1a	2.138(A)[d]	$J_{AY} = J_{BX} = -13.28$	49.40	2.327(AA′)[e]	$J_{AX} = J_{A'XN} = -13.40$	51.78
	2.141(B)[d]	$J_{AX} = 5.48$; $J_{AB} = 1.48$			$J_{AA'} = 5.09$; $J_{AX'} = 6.48$	
b	2.640(X)[d]	$J_{BY} = 5.01$		2.527(XX′)[e]	$J_{A'X} = 6.71$	
	2.647(Y)[d]	$J_{XY} = 12.35$			$J_{XX'} = 5.70$	
3a	2.214 dd	13.1(3b); 9.8(4)	61.19	2.166 dd	13.2(3b); 10.2(4)	61.92
b	2.272 dd	13.1(3a); 2.7(4)		2.395 dd	13.2(3a); 2.6(4)	
4	3.763 dqd	9.8(3a); 6.2(5); 2.7(3b)	63.80	3.724 dqd	10.2(3a); 6.4(5); 2.6(3b)	64.32
5	1.051 d	6.2(4)	20.00	1.046 d	6.4(4)	19.88
9a	3.347 d	13.7(9b)	54.15	3.393 d	13.7(9b)	53.70
b	3.499 d	13.7(9a)		3.458 d	13.7(9a)	
11			82.15			82.41
12	4.13		70.47	4.13		70.47
13			68.33			68.26
14			67.87			67.98
15	4.02		70.06	4.02		70.00
16−18	4.070 s		68.49	4.070		68.49

[a] In $CDCR_3$. [b] ^{1}H chemical shift. Letters refer to the coupling pattern s = singlet, d = doublet, and q = quartet. [c] (^{1}H,^{1}H) coupling constants. The numbers in parentheses indicate the position to which the proton is coupled. [d] ABXY spin system. Values obtained from a computor analysis. [e] AA′XX′ spin system. Values obtained from a computer analysis.

for the Re═O stretching frequency in **2** which is observed at 917 cm^{-1}. This frequency is much lower than expected (960−980 cm^{-1})[28] but compares well with the reported value of 915 cm^{-1} obtained for [ReO(L-*N₃O₂*)] (L-*N₃O₂* = *N*,*N*′-bis(salicylideneiminato)pentylene-1,5-diamine).[29] The molecular structure of the latter displays a Re═O bond length that is the same as that recorded for **2**.

The ^{1}H and ^{13}C NMR data of **1** (Table 2, Figure 1) confirm the symmetry of the molecule around the carbon−carbon bond of the $N-CH_2-CH_2-N$ moiety and show that **1** exists in solution as two interconverting isomers with a ratio of ca. 70:30 in $CDCl_3$. The ratio of the minor isomer increased when the ^{1}H NMR spectrum of **1** was recorded in more polar solvents such as acetone-*d*₆ and DMSO-*d*₆. At higher temperature (90 °C) this isomer predominates in DMSO-*d*₆. The assignment of the NMR resonances is straightforward. The carbon atoms of the substituted Cp rings were assigned on the basis of the observation that the ^{13}C resonance of the carbon atoms of the unsubstituted Cp ring is found downfield from the chemical shifts of the β-carbon atoms and upfield from the α-carbon atoms of the substituted Cp ring.[30] All proton−proton couplings (except for the Cp rings) of both isomers of **1** in $CDCl_3$ have been obtained. Identical ^{1}H NMR values were obtained by computer analysis for the complex spin system, resulting from the $N-CH_2-CH_2-N$ protons from the ^{1}H NMR spectra recorded at 500 or 300 MHz. For the major isomer of **1** in $CDCl_3$ the chemical shift differences between the $N-CH_2-CH_2-N$ protons and also the C(9) protons are larger than those observed for the minor isomer. Nuclear Overhauser effects (NOE's) are observed between the $N-CH_2-CH_2-N$ protons and the $CH_2(3)$ protons of the major isomer, which was not observed for the minor isomer. According to these results and especially the values obtained for the vicinal proton−proton coupling constants between the protons of the $N-CH_2-CH_2-N$ moiety, it appears that the minor isomer of **1** in $CDCl_3$ has a random conformation while the major isomer is highly restricted probably because of hydrogen bonding between the OH groups. This phenomenon is being further investigated.

The ^{1}H, ^{13}C, and ^{31}P NMR data of **2** are summarized in Table 3 with the same numbering system as used in the crystal structure determination. The designation of a and b for the protons of the methylene groups $CH_2(1)$, $CH_2(2)$, $CH_2(3)$, and $CH_2(6)$ refers to the exo and endo orientations with respect to the Re═O bond, respectively. Very little overlap occurs between the signals of the protons on the heterocyclic rings in the ^{1}H NMR spectrum recorded of **2** dissolved in $CDCl_3$. Assignment of the proton signals can, therefore, easily be accomplished from the cross-peaks observed in a correlation spectroscopy (COSY) experiment (see Table 3). Correlations resulting from geminal and vicinal coupling constants were used to connect protons within a heterocyclic ring, whereas correlations resulting from proton−proton couplings over more than three bonds were used to connect protons across the heterocyclic rings. Cross-peaks observed between H(1a) and H(9b) and between H(6a) and H(9a) allowed a distinction between $CH_2(9)$ and $CH_2(20)$. Correlations observed in the COSY experiments between the $CH_2(20)$ methylene protons and resonances arising from the protons of one of the substituted Cp rings resulted in the unambiguous assignment of all proton resonances, except for the unsubstituted Cp rings, to specific protons. The ^{13}C NMR resonances were assigned by correlating them to the assigned proton resonances using a heteronuclear multiple-quantum coherence (HMQC) experiment. The two aliphatic quaternary carbon resonances were assigned with heteronuclear multiple-bond correlation (HMBC) experiments. The correlations observed during the HMBC experiment, which resulted from (C,H) coupling constants over more than one bond, supply additional proof for the assignment of the substituted Cp ring protons and ^{13}C resonances (see Table 3).

The relative orientation of the two similar moieties of **2** [$CH_3(5)-CH(4)-CH_2(3)\cdots$ and $CH_3(8)-CH(7)-CH_2(6)\cdots$] to the PPh_3 group has been established with a rotating-frame Overhauser enhancement spectroscopy (ROESY) experiment in which NOE correlations were observed inter alia between the aromatic resonances and H(3a), H(20b), and H(25).

The overriding result of the NMR data is the rigidity of complex **2** in solution. This is especially indicated by the big vicinal proton−proton coupling constants observed between

---

(28) Roncari, E.; Mazzi, U.; Rossi, R.; Duatti, A.; Magon, L. *Transition Met. Chem.* **1981**, *6*, 169−173.

(29) Tisato, F.; Refosco, F.; Mazzi, U.; Bandoli, G.; Nicolini, M. *Inorg. Chim. Acta* **1991**, *189*, 97−103.

(30) (a) Azizian, J.; Roberts, K. M. G.; Silver, J. *J. Organomet. Chem.* **1986**, *303*, 397−409. (b) Koridze, A. A.; Petrovskii, P. V.; Mokhou, A. J. *J. Organomet. Chem.* **1977**, *136*, 57−63.

Table 3. ^{1}H, ^{13}C, and ^{31}P NMR Data[a] for ReO[(L-N_2O_2)(PPh$_3$)]PF$_6$ (**2**)

proton/carbon	δ_H[b] (ppm)	J(HH)[c] (Hz)	COSY[d]	δ_C[e] (ppm)	J(CP)[f] (Hz)	HMBC[g]
1a	2.526 td	14.3(1b); 14.3(2b); 3.9(2a)	1b, 2a, 2b, 9b	60.50		
b	3.608 dt	14.3(1a); 4.1(2b) 4.1(P)	1a, 2b			9
2a	3.036 dd	14.5(2b); 4.1(1b)	1a, 2b	67.32		
b	3.403 ddd	14.5(2a); 14.3(1a); 4.1(1b)	1a, 1b, 2a, 3a			1
3a	2.180 ddd	12.0(3b); 10.9(4); 1.4(2b)	2b, 3b, 4	71.27		
b	3.153 dd	12.0(3a); 4.8(4)	*i*			
4	4.016 m		3a, 3b, 5	77.13		
5	0.512 d	6.0(4)	4	20.54		
6a	2.494 ddd	12.2(6b); 11.4(7); 0.7(9a)	6b, 7, 9a	67.23		7, 9
b	3.150 ddd	12.2(6a); 2.9(7); 2.7(P)	*i*			
7	5.503 dqd	11.4(6a); 6.2(8); 2.9(6b)	6a, 6b, 7	93.66	4.8	
8	1.505 d	6.2(7)		20.67		6, 7
9a	4.077 d	14.4 (9b)	6a, 9b	58.19		10
b	4.399 d	14.4 (9a)	1a, 9a			1, 11, 14
10				77.31		
11	4.454 m			72.07		10, 12
12	4.347 m			70.21		
13	4.321 m			69.90		
14	4.341 m			71.47		10, 13
15−19[h]	4.256 s			69.32		
20a	3.110 d	14.2(20b)	20b, 22, 23	67.32		21, 22, 25
b	3.989 d	14.2(20a)	20a, 25			21, 22, 25
21				77.61		
22	4.287 m			71.19		21, 23, 24
23	4.206 m			69.88		
24	4.089 m			69.06		
25	3.562 m		22, 23, 24	70.73		21, 23, 24
26−30[h]	4.052 s			68.80		
arm. o	7.834 m			134.48	10.6	
m	7.556 m			128.93	10.6	
p	7.556 m			131.72		
ipso				132.53	49.9	

[a] ^{31}P chemical shift for PPh$_3$ = −7.60 ppm in CDCR$_3$. [b] ^{1}H chemical shifts. Letters refer to the coupling pattern s = singlet, d = doublet, t = triplet, and q = quartet. [c] (^{1}H,^{1}H) coupling constants. The numbers in parentheses indicate the position to which the proton is coupled. [d] Numbers refer to protons correlating with the proton given in column with the heading "proton". [e] ^{13}C chemical shifts. [f] (^{13}C,^{31}P) coupling constants. [g] Numbers refer to the carbon atoms correlating with the proton given in column with the heading "proton". [h] May be interchanged. [i] Overlap between H(3b) and H(6b).

Table 4. Selected Bond Lengths and Angles for H$_2$L (**1**)

	Bond Lengths (Å)		
O(1A)−C(7A)	1.323(9)	O(1B)−C(7B)	1.306(6)
O(1AA)−C(7A)	1.300(2)	O(1BB)−C(7B)	1.356(11)
O(2A)−C(4A)	1.420(6)	O(2B)−C(4B)	1.424(6)
C−C$_{av}$ (11A−15A)[a]	1.418(6)	C−C$_{av}$ (11B−15B)[a]	1.417(7)
C−C$_{av}$ (16A−20A)	1.412(7)	C−C$_{av}$ (16B−20B)	1.406(7)
C−C$_{av}$ (21A−25A)	1.413(7)	C−C$_{av}$ (21B−25B)	1.415(8)
C−C$_{av}$ (26A−30A)	1.404(9)	C−C$_{av}$ (26B−30B)	1.327(12)
Fe1A−C$_{av}$ (11A−15A)	2.038(5)	Fe1B−C$_{av}$ (11B−15B)	2.034(5)
Fe1A−C$_{av}$ (16A−20A)	2.038(5)	Fe1B−C$_{av}$ (16B−20B)	2.032(5)
Fe2A−C$_{av}$ (21A−25A)	2.032(5)	Fe2B−C$_{av}$ (21B−25B)	2.033(5)
Fe2A−C$_{av}$ (26A−30A)	2.027(6)	Fe2B−C$_{av}$ (26B−30B)	1.993(8)
	Bond Angles (deg)		
O(2A)−C(4A)−C(5A)	109.1(4)	O(2A)−C(4A)−C(5A)	108.2(4)
O(2A)−C(4A)−C(3A)	108.9(4)	O(2A)−C(4A)−C(3A)	108.8(4)
C(5A)−C(4A)−C(3A)	113.8(4)	C(5A)−C(4A)−C(3A)	113.5(4)
O(1AA)−C(7A)−C(6A)	125.9(9)	O(1AA)−C(7A)−C(6A)	124.9(6)
O(1A)−C(7A)−C(6A)	116.0(6)	O(1A)−C(7A)−C(6A)	115.4(5)
O(1AA)−C(7A)−C(8A)	121.2(9)	O(1AA)−C(7A)−C(8A)	114.7(6)
O(1A)−C(7A)−C(8A)	108.2(6)	O(1A)−C(7A)−C(8A)	107.1(5)

[a] Average C−C bond lengths of the Cp ring starting with the designated C atom.

H(1a) and H(2b) (14.3 Hz), H(3a) and H(4) (10.9 Hz), and H(6a) and H(7) (11.4 Hz). No vicinal coupling constant was detected between H(1a) and H(2a), indicating that the dihedral angle between these two protons must be highly restricted and close to 90°. The protons of the CH$_3$ groups, H(5) and H(8), were observed at 0.512 and 1.503 ppm with H(5) in proximity to the phenyl groups (from the ROESY results). These values are 0.5 ppm upfield and downfield compared to the same resonances in **1**. The methyl group CH$_3$(5) and also the neighboring protons must therefore be predominantly in the shielding zone of the phenyl rings. The methyl group CH$_3$(8) and the neighboring protons are deshielded probably by the phenyl rings and/or the anisotropy of the Re=O bond. The observation of signals for each of the CH groups of the Cp rings, as well as for each of the protons of the methylene groups CH$_2$(9) and CH$_2$(20), shows that even rotation of the ferrocenyl groups is restricted. The upfield signal at δ_H = 3.562 ppm observed for H(25) further proves the proximity of H(25) to the phenyl rings and the restricted motion of this moiety.

It is interesting to note that H(1b) and H(6b), which both have an exo relationship to the phosphorus atom, exhibited (^{1}H, ^{31}P) couplings. The couplings were confirmed in a ^{1}H{^{31}P} NMR experiment. A (^{13}C, ^{31}P) coupling of 4.8 Hz is also detected for C-7, which is trans to the phosphorus atom, while no such coupling is observed for C-4, gauche to the ^{31}P atom.

Both **1** and **2** were subjected to crystallographic studies to compare solid-state structures with the information obtained by NMR spectroscopy in solution. Selected bond distances and angles are represented in Tables 4 and 5. Figure 2 shows molecule **A**, which coexists with **B** in the unit cell of **1**. Molecule **A** differs in a few distinctive ways from molecule **B**. Apart from the different orientations in space, the orientations of the two Cp rings of the two ferrocenyl moieties in **A** are both in an eclipsed conformation for both cases while in **B** the conformation is eclipsed for one ferrocenyl unit and staggered for the other. This is probably a packing phenomenon. The planes of the Cp rings are orthogonally orientated for the two ferrocenyl

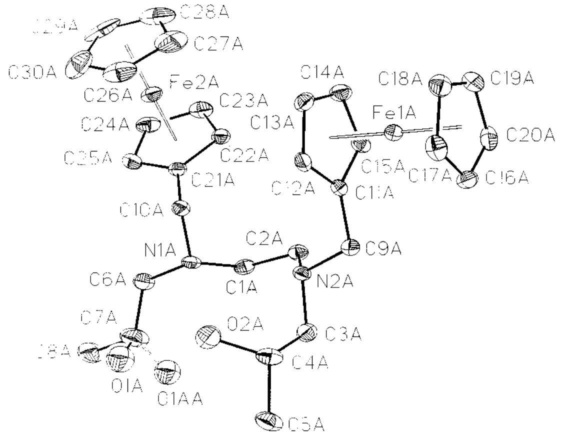


Figure 2. Molecular structure of **1(A)** with crystallographic atom numbering.

Table 5. Selected Bond Lengths and Angles for [ReO(L)(PPh$_3$)]PF$_6$ (**2**)

Bond Lengths (Å)			
Re−O(3)	1.714(5)	Re−O(1)	1.922(6)
Re−O(2)	1.929(5)	Re−N(1)	2.177(6)
Re−N(2)	2.292(6)	Re−P(1)	2.472(2)
Bond Angles (deg)			
O(3)−Re−O(1)	109.0(2)	O(3)−Re−O(2)	162.8(2)
O(1)−Re−O(2)	88.2(2)	O(3)−Re−N(1)	95.6(2)
O(1)−Re−N(1)	83.9(2)	O(2)−Re−N(1)	87.1(2)
O(3)−Re−N(2)	88.8(2)	O(1)−Re−N(2)	158.5(2)
O(2)−Re−N(2)	75.4(2)	N(1)−Re−N(2)	81.6(2)
O(3)−Re−P(1)	88.8(2)	O(1)−Re−P(1)	87.6(2)
O(2)−Re−P(1)	90.9(2)	N(1)−Re−P(1)	171.3(2)
N(2)−Re−P(1)	106.1(2)		

units in each molecule. These rings are coplanar in molecules that contain a sequence of Fc−Fc−Fc units[31] or are separated by an even number of cummulene carbons.[32] The eclipsed conformation is favored in unsubstituted and monosubstituted ferrocene compounds, but in disubstituted complexes the staggered arrangement of the Cp rings is often encountered. A comparison of the structural data for ferrocene and some of its derivatives with [Pd(dppf-*P*,*P*′)(anthracenyl)Br][33] outlines these orientations. The chiral carbon atoms, C(4) and C(7), afford configurations corresponding to a racemic mixture of isomers, and the presence of the two independent molecules **A** and **B** in the crystal is due to the specific configuration of C(4) with respect to that of C(7).

The Fe−C bond lengths of the Cp rings fall in the range 1.980−2.046 Å, which are within the range reported for ferrocenyl ligands, for instance, [Fe{C$_5$H$_4$CH$_2$NHC$_6$H$_4$OH}Cp] with an average of 2.028 Å.[32a] One of the Cp rings, C(26B)−C(30B), displays different Fe−C and C−C bond distances, and these are significantly shorter than those of the other rings, which are all the same within experimental error. This ring is the unsubstituted ring of the ferrocenyl unit and is in the eclipsed conformation. It is clear that the Cp ring C(26B)−C(30B) is closer to the iron atom and also displays shorter intra-ring C−C bond lengths. The C−C−C bond angles of the Cp rings, which average 108.0(7)° with an extreme spread of 105.1−111.0°, are less than the corresponding range of 87.8−121.1° reported for comparable ferrocenyl ligands.[34]

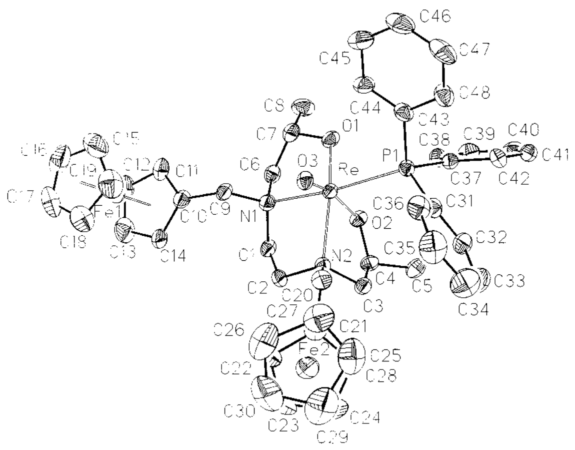


Figure 3. Molecular structure of the cation of **2** with atom numbering.

The greatest disorder in the molecule is centered around the chiral carbon C(7). The positioning of the oxygen atom at C(7) was allowed to float, while the oxygen position was fixed at C(4). In **A** the bond lengths of O(1A)−C(7A) (1.323(9) Å) and O(1AA)−C(7A) (1.30(2) Å) are significantly shorter than the O(2A)−C(4A) bond length of 1.420(6) Å despite the larger standard deviations. This is also true for molecule **B** where O(1B)−C(7B) and O(1BB)−C(7B) are shorter than O(2B)−C(4B). The disorder is also manifested in the angles around especially C(7). The O(1A)−C(7A)−C(6A) (116.0(6)°), O(1AA)−C(7A)−C(6A) (125.9(9)°), and O(2AA)−C(7A)−C(8A) (121.2(9)°) bond angles are larger than the ideal angle of ca. 109°, as is observed for O(1A)−C(7A)−C(8A) (108.2(6)°), O(2A)−C(4A)−C(3A) (108.9(4)°), and O(2A)−C(4A)−C(5A) (109.1(4)°).

Figure 3 depicts the molecular structure of the cation of **2** together with the atom numbering scheme used. The complex geometry around the Re atom in **1** is that of a highly distorted octahedron with the oxo ligand and one of the pendant oxygen atoms of the N_2O_2 ligand coordinated in trans positions. The four corners of the perpendicular equatorial plane are spanned by two nitrogen and one oxygen atom of the N_2O_2 ligand, while the remaining position is occupied by the coordinated PPh$_3$ ligand. The PF$_6^-$ ion acts as the counterion.

The Re═O (Re−O(3)) bond length of 1.714(5) Å is longer than the bond lengths observed for similar six-coordinate Re(V) complexes, where bond lengths of 1.68−1.69 Å were found,[17b,35] except for the complexes [ReO(N_3O_2)]·MeOH (N_3O_2 = *N*,*N*′-bis(salicylideneiminato)pentylene-1,5-diamine)[17b,35] and [ReO(salphos)Cl$_2$][36] in which the Re═O bonds are 1.72(1) and 1.71(1) Å, respectively. The Re−O(1) and Re−O(2) bond lengths of 1.922(6) and 1.926(6) Å are within, but on the shorter side of, the expected range for Re−O bond lengths. Distances of between 1.92 and 2.14 Å for Re−O single bonds cis with respect to the Re═O bond and 1.92−2.09 Å for bonds trans to the Re═O bond are documented.[35,36] The Re−N(1) bond length of 2.177(6) Å is much shorter than the Re−N(2) bond length of 2.292(6) Å. This is expected because the phosphorus atom trans to the N(1) atom, unlike the N(2) atom that is trans to an

---

[31] (a) Dond, T.-Y.; Lee, W.-Y.; Su, P. T.; Chang, L.-S.; Lin, K.-J. *Organometallics* **1998**, *17*, 3323−3330. (b) Rodriques, J.-G.; Oñate, A.; Martin-Villamil, R. M.; Fonseca, I. *J. Organomet. Chem.* **1996**, *513*, 71−76.

[32] Bildstein, B.; Schweiger, M.; Kopacka, H.; Ongania, K.-H.; Wurst, K. *Organometallics* **1998**, *17*, 2414−2424.

[33] Butler, I. R.; Hobson, L. T.; Coles, S. T.; Hursthouse, M. B.; Abdul-Malik, K. M. *J. Organomet. Chem.* **1997**, *540*, 27−40.

[34] Benito, A.; Cano, J.; Martínez-Máñez, R.; Soto, I.; Tendero, M. J. L.; Payá, J.; Sinn, E. *Inorg. Chim. Acta* **1993**, *210*, 233−236.

[35] Connac, F.; Lucchese, Y.; Dartiguenave, M.; Beauchamp, A. L. *Inorg. Chem.* **1997**, *36*, 256−259.

[36] Banbery, H. J.; Hussain, W.; Hamor, T. A.; Jones, C. J.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1990**, 657−661.

oxygen atom, is capable of withdrawing electron density from the N(1) atom via π-interaction. The N(1) bond length is on the long end of the range for Re−N bonds, with the Re−N(2) bond falling outside the range reported for Re−N bond lengths. This is in a sense expected as a result of the crowding between the cis-orientated PPh_3 ligand and the ferrocenyl group on N(2) that will cause bond lengthening and a P−Re−N(2) angle of 106.1(2)°, which represents a significant distortion from 90°. The effect of this crowding is evident in the observed angles for N(2)−Re−N(1), N(2)−Re−O(1), and O(1)−Re−P of 81.6(2), 83.9(2), and 87.6(2)°, respectively, instead of the ideal values of 90°. The extreme distortion experienced by the N(2) atom is also noted in the large deviation from the ideal 90° and 180° bond angles for N(2)−Re−O(2) and N(2)−Re−O(1) of 75.4(2)° and 158.5(2)°, respectively. However, the Re−P bond length of 2.472(2) Å is the same as for other six-coordinate Re(V) complexes containing a PPh_3 ligand.[24] The distortion experienced by the N(1) atom is also evident in the bond angle of 95.6(2)° of the N(1)−Re−O(3) angle.

The configurations of the C(4) and C(7) atoms are both determined as *S*, and the conformation of the three five-membered chelate rings corresponds to ReN(1)C(6)C(7)O(1) and Re(N(2)C(3)C(4)O(2) displaying δ-conformations and the ReN(1)C(1)C(2)N(2) ring having a λ-conformation.[37] The conformation of the Cp rings of the ferrocenyl moiety in both rings is gauche. The bulkiness of the PPh_3 ligand, the strained chelate rings, and the ferrocenyl substituents affect the positions around the rhenium center in such a manner that the only relatively "open" site in the complex is in the vicinity of the Re═O bond. Especially crowded is the area taken up by the PPh_3 ligand and ferrocenyl group (2), resulting in the latter being pushed away from the Re atom. All other C−C and Fe−C bond lengths and angles in the ferrocenyl moieties, as well as the bond angles, are in good agreement with those found for **1**.

Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of 1,6-diferrocenyl-*N,N′*-bis-(2-hydroxypropyl)-2,5-diazahexane (**1**) and (*N,N′*-bis(ferrocenylmethyl)-4,7-diazadecane-2,9-dioxo-N_2O_2)triphenylphosphineoxorhenium(V) hexafluorophosphate (**2**). This material is available free of charge via the Internet at http://pubs.acs.org.

IC000746Y

---

[37] Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354−1358.