Inorganica Chimica Acta, 213 (1993) 247–251

Reactions of the electron-rich triply bonded dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br) with dioxygen

Part III*. The isolation and structural characterization of the dirhenium(V) complex $Re_2(\mu\text{-O})_2(O)_2Cl_2(\mu\text{-dppm})_2$

Keng-Yu Shih, Phillip E. Fanwick and Richard A. Walton**

Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393 (USA)

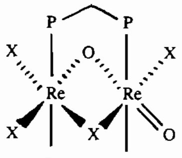
(Received May 5, 1993)

Abstract

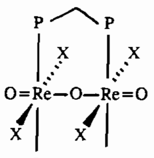
The complex $Re_2(\mu\text{-O})(O)_2Cl_4(\mu\text{-dppm})_2$ converts to the closely related tetraoxo dirhenium(V) species $Re_2(\mu\text{-O})_2(O)_2Cl_2(\mu\text{-dppm})_2$ in dichloromethane in the presence of amines such as NEt_3 and pyridine. This reaction can be reversed upon reacting $Re_2(\mu\text{-O})_2(O)_2Cl_2(\mu\text{-dppm})_2$ with thionyl chloride. A structural analysis of $Re_2(\mu\text{-O})_2(O)_2Cl_2(\mu\text{-dppm})_2$ shows it to have an edge-sharing bioctahedral structure with a very long Re···Re distance (3.1237(7) Å). This is the first example of a structurally characterized $[Re_2O_4]^{2+}$ species in which there is a planar centrosymmetric $ORe(\mu\text{-O})_2ReO$ unit. Crystal data for $Re_2(\mu\text{-O})_2(O)_2Cl_2(\mu\text{-dppm})_2 \cdot 4CH_2Cl_2$ at −70 °C: triclinic space group $P\bar{1}$ (No. 2), $a = 9.769(3)$, $b = 12.269(4)$, $c = 13.128(6)$ Å, $\alpha = 96.59(4)$, $\beta = 107.92(4)$, $\gamma = 93.09(3)°$, $V = 1480(2)$ Å^3, $Z = 1$. The structure was refined to $R = 0.040$ ($R_w = 0.050$) for 3388 data with $I > 3\sigma(I)$.

Introduction

In a recent examination [2] of the behavior of the triply bonded dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br; dppm = $Ph_2PCH_2PPh_2$) [3–5] towards dioxygen, we discovered that net 4- and 6-electron redox reactions occur to form the compounds $Re_2(\mu\text{-O})(\mu\text{-X})(O)X_3(\mu\text{-dppm})_2$ (**1**) and $Re_2(\mu\text{-O})(O)_2X_4(\mu\text{-dppm})_2$ (**2**) in which a metal–metal bond is no longer present. Such a sequence of oxygenation reactions has not been reported previously for multiply bonded dimetal complexes [6, 7]. We are now in the process of examining the chemistry of the products **1** and **2**, and in the present report describe the conversions of **1a** and **2a** to the tetraoxodirhenium(V) complex $Re_2(\mu\text{-O})_2(O)_2Cl_2(\mu\text{-dppm})_2$ (**3**) which is only the second example of a structurally characterized $[Re_2O_4]^{2+}$ complex that contains an edge-sharing bioctahedral geometry. Details of the properties and single crystal X-ray structure of this complex are provided.



1a: X = Cl
b: X = Br



2a: X = Cl
b: X = Br

Experimental

Starting materials and reaction procedures

The complex $Re_2Cl_4(\mu\text{-dppm})_2$ was prepared as described in the literature [4, 5] and converted to $Re_2(\mu\text{-O})(\mu\text{-Cl})(O)Cl_3(\mu\text{-dppm})_2$ (**1a**) and $Re_2(\mu\text{-O})(O)_2Cl_4(\mu\text{-dppm})_2$ (**2a**) following reported procedures [1]. Solvents and bases such as triethylamine and other amines were obtained from commercial sources and dried and deoxygenated prior to use in the usual way [2]. All reactions were performed under an atmosphere of dinitrogen with standard Schlenk techniques.

A. Synthesis of $Re_2(\mu\text{-O})_2(O)_2Cl_2(\mu\text{-dppm})_2$

(i) From **2a**. A solution of **2a** (0.05 g, 0.038 mmol) in dichloromethane (3 ml) was treated with a small quantity of freshly distilled triethylamine (0.07 ml) and the mixture stirred at room temperature for 6 h. After this time, the brown precipitate was filtered off, washed with diethyl ether (3×5 ml), and dried under vacuum; yield 0.03 g (63%). *Anal.* Calc. for $C_{50}H_{44}Cl_2O_4Re_2$: C, 47.06; H, 3.50. Found: C, 46.74; H, 3.20%.

---

*For Part II see ref. 1.

**Author to whom correspondence should be addressed.

0020-1693/93/$6.00

This same reaction occurs when other bases are used in place of triethylamine, specifically, t-BuNH$_2$, (i-Pr)$_2$EtN, 2-Etpy, 2,5-Et$_2$py, 2-NH$_2$py, 2,6-Me$_2$py or K[N(SiMe$_3$)$_2$].

(ii) From **1a**. With the use of a procedure similar to that described in A (i) but with **1a** (0.05 g, 0.038 mmol) in place of **2a**, a small quantity of **3** was filtered off after a reaction time of 18 h; yield 0.005 g (10%). The properties of this product were identical in all respects with those of the samples of **3** prepared from **2a**.

B. Conversion of 3 to 2a

A suspension of Re$_2$(μ-O)$_2$(O)$_2$Cl$_2$(μ-dppm)$_2$ (0.04 g, 0.031 mmol) was stirred in 5 ml of CH$_2$Cl$_2$ and treated with a small quantity of thionyl chloride (0.02 ml). This mixture rapidly changed color from brown to bright green and the resulting solution was stirred at room temperature for 5 min and then treated with diethyl ether (30 ml) to induce precipitation of the product. The green powder was filtered off, washed with diethyl ether (3×3 ml), and dried under vacuum; yield 0.035 g (83%). The identity of this product was confirmed by a comparison of its electrochemical and spectroscopic properties with those of an authentic sample of **2a** [2].

Preparations of single crystals of 3 for an X-ray structure analysis

A solution of **3** in dichloromethane was exposed to diisopropyl ether vapor for several days. Suitable crystals were obtained by this method but because lattice solvent was rapidly lost at room temperature the crystal structure was determined at low temperature.

X-ray crystallography

The structure of **3** was determined at −70 °C by the application of standard procedures. The basic crystallographic parameters for this complex are listed in Table 1. The cell constants are based on 25 reflections with $20<\theta<23°$. Three standard reflections were measured after 5000 s of beam time during data collection; there were no systematic variations in intensity. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package. The crystal was found to belong to the triclinic space group $P\bar{1}$ (No. 2). Lorentz and polarization corrections were applied to the data. An empirical absorption correction [8] was applied, but no correction for extinction was made.

The structure was solved by the use of the Patterson heavy atom method which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were identified in succeeding difference Fourier syntheses. The atoms of two crystallographically independent molecules of lattice CH$_2$Cl$_2$ are located about general positions. Hydrogen atoms of the dppm ligands were introduced at calculated positions (C–H = 0.95 Å, $B=1.3$ B_c), not refined but constrained to ride on their C atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters, corrections for anomalous scattering being applied to these atoms [9].

TABLE 1. Crystallographic data and data collection parameters for Re$_2$(μ-O)$_2$(O)$_2$Cl$_2$(μ-dppm)$_2$·4CH$_2$Cl$_2$ (**3**)

Formula	Re$_2$Cl$_{10}$P$_4$O$_4$C$_{54}$H$_{52}$
Formula weight	1615.84
Space group	$P\bar{1}$ (No. 2)
a (Å)	9.769(3)
b (Å)	12.269(4)
c (Å)	13.128(6)
α (°)	96.59(4)
β (°)	107.92(4)
γ (°)	93.09(3)
V (Å^3)	1480(2)
Z	1
D_c (g cm^{-3})	1.812
Crystal dimensions (mm)	0.40×0.30×0.13
Temperature (°C)	−70
Radiation (wavelength)	Mo Kα (0.71073 Å)
Monochromator	graphite
Linear absorption coefficient (cm^{-1})	47.45
Absorption correction applied	empirical^a
Transmission factors: min., max.	0.55, 1.00
Diffractometer	Enraf-Nonius CAD4
Scan method	ω–2θ
h, k, l limits	−10 to 9, −13 to 13, 0 to 14
2θ Range (°)	4.00–45.00
Scan width (°)	0.82 + 0.35 tan(θ)
Take-off angle (°)	2.95
Programs used	Enraf-Nonius MolEN
F(000)	788.0
p-Factor used in weighting	0.040
Data collected	3877
Unique data	3877
Data with $I>3.0\sigma(I)$	3388
No. variables	334
Largest shift/e.s.d. in final cycle	0.01
R^b	0.040
$R_w{}^c$	0.050
G.O.F.^{d}	1.638

^{a}See ref. 8. $^bR=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^cR_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=1/\sigma^2(F_o)$. ^{d}Goodness of fit $=[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{parameters})]^{1/2}$.

Positional parameters and their errors for all non-hydrogen atoms are listed in Table 2. Important intramolecular bond distances and angles are given in Table 3. See also 'Supplementary material'.

Physical measurements

A Perkin-Elmer 1800 FTIR spectrometer was used to record the IR spectra of the compounds as mineral

TABLE 2. Positional parameters for the non-hydrogen atoms of **3** and their e.s.d.s[a]

Atom	x	y	z	B (Å^2)
Re	0.06967(3)	0.38858(3)	0.01153(3)	1.727(6)
Cl	0.2326(2)	0.3042(2)	−0.0705(2)	2.90(5)
P(1)	0.2736(2)	0.4859(2)	0.1615(2)	1.87(4)
P(2)	0.1532(2)	0.7088(2)	0.1265(2)	2.26(5)
O(B)	0.0615(5)	0.5100(4)	−0.0659(4)	1.6(1)
O(T)	0.0552(6)	0.2904(5)	0.0917(4)	2.5(1)
C(B)	0.3067(9)	0.6266(7)	0.1369(7)	2.2(2)
C(111)	0.2495(9)	0.4946(7)	0.2941(6)	2.3(2)
C(112)	0.356(1)	0.5525(8)	0.3830(8)	3.2(2)
C(113)	0.342(1)	0.560(1)	0.4847(8)	4.4(3)
C(114)	0.222(1)	0.508(1)	0.4981(8)	5.0(3)
C(115)	0.114(1)	0.451(1)	0.4090(8)	4.7(3)
C(116)	0.1275(9)	0.4460(9)	0.3085(7)	3.3(2)
C(121)	0.4468(8)	0.4291(7)	0.1838(6)	2.1(2)
C(122)	0.5642(9)	0.4796(8)	0.1622(7)	2.7(2)
C(123)	0.6910(9)	0.4294(8)	0.1796(8)	3.2(2)
C(124)	0.701(1)	0.3291(9)	0.2153(8)	3.7(2)
C(125)	0.585(1)	0.2762(8)	0.2345(8)	3.6(2)
C(126)	0.4580(9)	0.3265(8)	0.2178(8)	3.1(2)
C(211)	0.163(1)	0.7535(8)	0.2651(8)	2.9(2)
C(212)	0.060(1)	0.7151(9)	0.3072(8)	3.4(2)
C(213)	0.072(1)	0.748(1)	0.4132(8)	4.4(3)
C(214)	0.187(1)	0.819(1)	0.4790(9)	5.0(3)
C(215)	0.292(1)	0.858(1)	0.440(1)	5.3(3)
C(216)	0.280(1)	0.8250(9)	0.3339(9)	4.0(3)
C(221)	0.208(1)	0.8329(7)	0.0819(7)	2.6(2)
C(222)	0.297(1)	0.8330(9)	0.019(1)	5.6(3)
C(223)	0.331(2)	0.927(1)	−0.021(1)	7.1(3)
C(224)	0.276(1)	1.0216(9)	0.002(1)	5.3(3)
C(225)	0.189(2)	1.0236(9)	0.064(1)	6.7(4)
C(226)	0.152(1)	0.929(1)	0.101(1)	6.6(3)
Cl(1001)	0.3185(4)	0.2558(3)	0.6571(4)	7.4(1)
Cl(1002)	0.3837(4)	0.0443(3)	0.7288(3)	7.4(1)
Cl(2001)	0.3228(7)	0.1485(5)	0.3829(5)	13.5(2)
Cl(2002)	0.0176(6)	0.0932(6)	0.3349(5)	14.7(2)
C(1000)	0.247(1)	0.131(1)	0.683(1)	6.7(4)
C(2000)	0.153(2)	0.156(2)	0.312(2)	16.8(8)

[a]Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1)+b^2\beta(2,2)+c^2\beta(3,3)+ab(\cos\gamma)\beta(1,2)+ac(\cos\beta)\beta(1,3)+bc(\cos\alpha)\beta(2,3)]$.

TABLE 3. Some important bond distances (Å) and bond angles (°) for **3**[a]

Distances			
Re–Re′	3.1237(7)	Re–O(B)	1.890(5)
Re–Cl	2.396(2)	Re′–O(B)	2.057(5)
Re–P(1)	2.462(2)	Re–O(T)	1.715(6)
Re–P(2)	2.500(2)		
Angles			
Re′–Re–Cl	131.72(6)	P(1)–Re–P(2)	173.66(8)
Re′–Re–P(1)	88.62(5)	P(1)–Re–O(B)	90.8(2)
Re′–Re–P(2)	89.67(5)	P(1)–Re–O(T)	89.2(2)
Re′–Re–O(T)	129.8(2)	P(2)–Re–O(B)	87.8(2)
Cl–Re–P(1)	90.96(8)	P(2)–Re–O(T)	87.2(2)
Cl–Re–P(2)	94.73(8)	O(B)–Re–O(B)′	75.4(2)
Cl–Re–O(B)	92.2(2)	O(B)–Re–O(T)	169.4(3)
Cl–Re–O(T)	98.4(2)	Re–O(B)–Re′	104.6(2)

[a]Numbers in parentheses are e.s.d.s in the least significant digits.

oil (Nujol) mulls. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a}+E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions $E_{1/2}=+0.47$ V versus Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were performed with a BAS Inc. model CV-27 instrument in conjunction with a BAS model RXY recorder. NMR spectra were recorded on CD_2Cl_2 or $CDCl_3$ solutions of the complexes. The $^{31}P\{^1H\}$ spectra were obtained with use of a Varian XL-200A spectrometer operated at 80.98 MHz with 85% H_3PO_4 as an external standard. ^1H NMR spectra were obtained on a GE QE-300 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent.

Elemental microanalyses were performed by Dr H.D. Lee of the Purdue University Microanalytical Laboratory.

Results and discussion

The conversion of $Re_2(\mu\text{-}O)(O)_2Cl_4(\mu\text{-dppm})_2$ (**2a**) to $Re_2(\mu\text{-}O)_2(O)_2Cl_2(\mu\text{-dppm})_2$ (**3**) in the presence of nitrogen bases involves the exchange of one oxo group for two halogen atoms but no net oxidation state change. In the absence of added base, **2a** is unreactive under the reaction conditions we used. Complex **3** can also be formed from the lower valent compound $Re_2(\mu\text{-}O)(\mu\text{-}Cl)(O)Cl_3(\mu\text{-dppm})_2$ (**1a**) under these same conditions, but only in very low yield (10% or less). We believe that the latter reaction actually proceeds through the intermediate formation of small amounts of **2a** that are produced by the reaction of **1a** with trace amounts of O_2 that must still be present in the system. We have previously demonstrated [2] the effectiveness of **1a** as a scavenger for O_2 to form **2a**.

The IR spectrum (Nujol mull) of **3** shows very characteristic ν(Re=O) modes at 908(s) and 899(s) cm^{-1} and ν(Re–O–Re) at 787(s) and 780(s) cm^{-1}, as well as ν(Re–Cl) at 307(m-s) cm^{-1}. The ^1H NMR spectrum (recorded in $CDCl_3$) is very simple, with a binomial pentet at $\delta+3.58$ (–CH_2– of dppm, 4H) and phenyl resonances at $\delta+7.17$ (m, 24H), $+7.55$ (s, 8H) and $+7.70$ (s, 8H), while a singlet is present in the $^{31}P\{^1H\}$ NMR spectrum ($\delta-24.5$ in CD_2Cl_2, $\delta-24.7$ in $CDCl_3$). A cyclic voltammogram of a solution of **3** in 0.1 M

TBAH–CH_2Cl_2 (recorded at $\nu = 200$ mV s^{-1}) reveals the presence of an irreversible reduction at $E_{p,c} = -1.62$ V and an irreversible oxidation at $E_{p,a} = +0.76$ V versus Ag/AgCl, with the latter process having a weak coupled reduction wave at $E_{p,c} = +0.11$ V when a switching potential of *c.* +1.0 V was used. The extension of the CV scan to more positive potentials shows the presence of coupled processes with $E_{p,a} = +1.33$ V and $E_{p,c} = +1.25$ V versus Ag/AgCl and $i_{p,a} \approx i_{p,c}$, that may arise from a chemical product that is formed following the irreversible oxidation at +0.76 V.

The structure of **3** was established from an X-ray structure analysis of a crystal of composition $Re_2(\mu\text{-}O)_2(O)_2Cl_2(\mu\text{-dppm})_2 \cdot 4CH_2Cl_2$. The dirhenium molecule has a crystallographically imposed inversion center. An ORTEP representation of **3** is shown in Fig. 1, while crystallographic data and important structural parameters are given in Tables 1–3. The structure is that of a centrosymmetric edge-sharing bioctahedron with an Re···Re distance (3.1237(7) Å) that accords with the absence of a direct Re–Re interaction. The terminal and bridging Re–O distances in the *trans* O=Re–O units (1.715(6) and 1.890(5) Å, respectively) are very similar to those present in $Re_2(\mu\text{-}O)(O)_2Cl_4(\mu\text{-dppm})_2$ (**2a**) [2]. The major structural asymmetry in **3** arises because of the presence of pairs of short and long Re–O (bridging) bonds; these are a consequence of whether they are *trans* to an oxo or a chloro group.

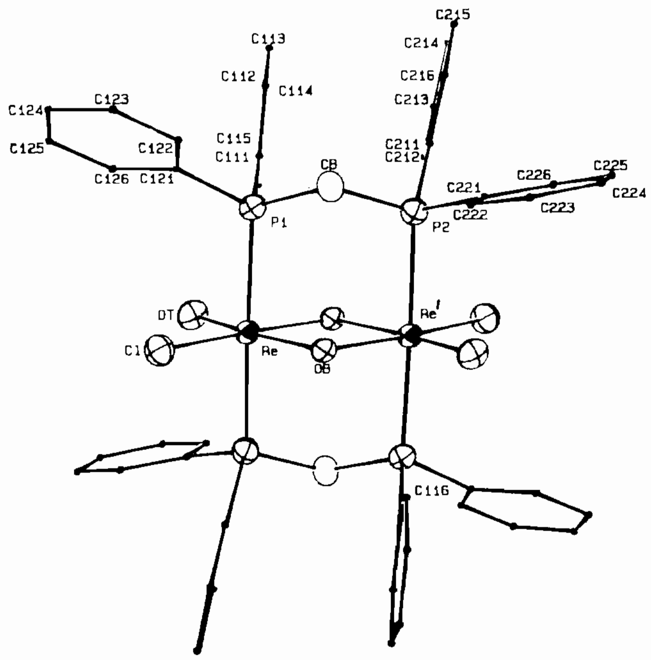


Fig. 1. ORTEP representation of the structure of the molecule $Re_2(\mu\text{-}O)_2(O)_2Cl_2(\mu\text{-dppm})_2$ (**3**). The thermal ellipsoids are drawn at the 50% probability level except for the phenyl carbon atoms which are circles of arbitrary radius.

The only other structurally characterized $[Re_2O_4]^{2+}$ complex that contains an edge-sharing bioctahedral geometry compound is the salt $[Re_2(\mu\text{-}O)_2(O)_2(L)_2]I_2$, where L represents the tridentate 1,4,7-triazacyclononane ligand [10]. This complex differs from **3** in having its terminal Re=O bonds in a *syn* disposition to one another and in possessing a very short Re–Re distance (2.405(1) Å). Non-organometallic $[Re_2O_4]^{2+}$ complexes are otherwise unknown [11, 12], but a few organometallics that contain this moiety have been isolated recently. The series of compounds $(\eta^5\text{-}C_5Me_5)_2Re_2(\mu\text{-}O)_2(O)_2$, $(\eta^5\text{-}C_5Me_5)_2Re_2(\mu\text{-}O)_2(O)Cl_2$ and $(\eta^5\text{-}C_5Me_5)_2Re_2(\mu\text{-}O)_2Cl_4$ that was prepared by Herrmann *et al.* [13] is particularly noteworthy, although none possess an edge-sharing bioctahedral geometry. The tetraoxo unit is far less commonly encountered in dirhenium(V) chemistry than are $[Re_2O_3]^{4+}$ species.

While details of the mechanism for the conversion of **2a** to **3** remain to be elucidated, this reaction requires the presence of a base. Nitrogen bases were most commonly employed, but we also found that PMe_3 and $P\text{-n-}Pr_3$ gave similar results although the product proved to be a mixture of **3** (identified by its electrochemical properties) and another unidentified material. Since the conversion of **2a** to **3** is a non-redox process it does not appear that a disproportionation step is involved. The reaction may be a consequence of the base assisted hydrolysis of **2a** which results from the presence of small amounts of adventitious water. The conversion of **2a** to **3** can be reversed, essentially quantitatively, by the reaction of **3** with thionyl chloride (eqn. (1)), a reagent that has long been known [14] to be effective for the conversion of an M=O unit to MCl_2.

$$Re_2O_4Cl_2(dppm)_2 + SOCl_2 \longrightarrow Re_2O_3Cl_4(dppm)_2 + SO_2 \quad (1)$$

Supplementary material

Tables of positional parameters for the hydrogen atoms, anisotropic thermal parameters, full listings of bond distances and bond angles, and observed and calculated structure factors for **3** are available on request from R.A.W. Further details concerning the structure determination can be obtained from Dr P.E. Fanwick of this department.

Acknowledgements

Support from the National Science Foundation, through Grant No. CHE91-07578 to R.A.W. and Grant No. CHE86-15556 for the purchase of the microVAX II computer and diffractometer, is gratefully acknowledged.

References

1 K.-Y. Shih, P.E. Fanwick and R.A. Walton, *Inorg. Chim. Acta, 212* (1993) 23.

2 (a) S.L. Bartley, K.R. Dunbar, K.-Y. Shih, P.E. Fanwick and R.A. Walton, *J. Chem. Soc., Chem. Commun.*, (1993) 98; (b) *Inorg. Chem., 32* (1993) 1341.

3 J.R. Ebner, D.R. Tyler and R.A. Walton, *Inorg. Chem., 15* (1976) 833.

4 T.J. Barder, F.A. Cotton, K.R. Dunbar, G.L. Powell, W. Schwotzer and R.A. Walton, *Inorg. Chem., 24* (1985) 2550.

5 A.R. Cutler, D.R. Derringer, P.E. Fanwick and R.A. Walton, *J. Am. Chem. Soc., 110* (1988) 5024.

6 F.A. Cotton and R.A. Walton, *Multiple Bonds Between Metal Atoms,* Oxford University Press, Oxford, UK, 2nd edn., 1993.

7 F.A. Cotton and R.A. Walton, *Struct. Bonding (Berlin), 62* (1985) 1.

8 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A, 39* (1983) 158.

9 (a) D.T. Cromer, *International Tables for X-ray Crystallography,* Vol. IV, Kynoch, Birmingham, UK, 1974, Table 2.3.1; (b) for the scattering factors used in the structure solution see: D.T. Cromer and J.T. Waber, Table 2.2B.

10 G. Böhm, K. Wieghardt, B. Nuber and J. Weiss, *Angew. Chem., Int. Ed. Engl., 29* (1990) 787.

11 C.E. Holloway and M. Melnik, *Rev. Inorg. Chem., 10* (1989) 236–357, and refs. therein.

12 K.A. Conner and R.A. Walton, in *Comprehensive Coordination Chemistry,* Pergamon, Oxford, UK, 1987, Ch. 43, pp. 125–213, and refs. therein.

13 W.A. Herrmann, M. Floel, J. Kulpe, J.K. Felixburger and E. Herdtweck, *J. Organomet. Chem., 355* (1988) 297.

14 M. Pasquali, A. Torres-Filho and C. Floriani, *J. Chem. Soc., Chem. Commun.*, (1975) 534.