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Synthetic routes and structures of $[Rh(Hdmg)\{ClZn(C_2H_5OH)dmg\}(PPh_3)Cl]$, $[Rh(Hdmg)_2(PPh)_2]^+[Rh(Hdmg)_2(Cl)_2]^- \cdot 2CH_3OH$, and $[Rh(Hdmg)2(PPh_3)I] \cdot 0.5C_2H_5OH$ complexes

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Abstract

Treatment of $[Rh(Hdmg)_2(PPh_3)Cl]$ with zinc amalgam afforded a heterobimetallic compound $[Rh(Hdmg)(ClZndmg)(PPh_3)Cl]$ (**1a**) (Hdmg = monoanion of dimethylglyoxime). Crystallization of (**1a**) from a $CHCl_3/C_2H_5OH$ mixture led to the formation of $[Rh(Hdmg)\{ClZn(C_2H_5OH)dmg\}(PPh_3)Cl]$ (**1**). The X-ray crystal structure of **1** revealed that the ethanol molecule was built into the complex molecule through the oxygen atom coordinated to the zinc cation and a hydrogen bond involving one of the chloride ligands. Reduction of $[Rh(Hdmg)_2(PPh_3)Cl]$ with Zn/Hg, followed by treatment with a $CHCl_3/CH_3OH$ mixture, gave the complex salt $[Rh(Hdmg)_2(PPh_3)_2]^+[Rh(Hdmg)_2(Cl)_2]^- \cdot 2CH_3OH$ (**2**). The X-ray structure of **2** showed crystals formed by cations $[Rh(Hdmg)_2(PPh_3)_2]^+$ and anions $[Rh(Hdmg)_2Cl_2]^-$. The anion binds one CH_3OH molecule through a hydrogen bond involving the adjacent oxime atom. Reduction of $[Rh(Hdmg)_2(PPh_3)Cl]$ with zinc amalgam in the presence of CH_3I led to the compound $[Rh(Hdmg)_2(PPh_3)I] \cdot 0.5C_2H_5OH$ (**3**), which was characterized by X-ray crystallography.

Keywords: Rhodium; Rhodoximes; Oximates; Spectral properties; Crystal structures

1. Introduction

The coordination environments of metal ions in biomolecules often consist of nitrogen donor atoms. Complexes of rhodium with the tetradentate equatorial ligand bisdimethylglyoximate $(Hdmg)_2$, called rhodoximes, are interesting analogues of cobaloximes, which are often considered to be models of vitamin B_{12} coenzyme [1]. Reactions of rhodoximes with alkyl halides are of considerable interest [2], as they contribute to a better understanding of the mechanistic and kinetic behaviour of these compounds [3]. Some rhodoximes have demonstrated very promising catalytic properties in hydrogenation [4a–4d], hydroformylation [4d], hydrosililation [5], and oxidation [6] reactions.

A good number of six-coordinate rhodoximes $[Rh(Hdmg)_2LX]$ (Fig. 1a) have already been studied [2,3,7]. Some metal complexes with planar, tetradentate chelating ligands are able to form different adducts. The bridging hydrogen of the equatorial $O-H\cdots O$ groups can be substituted by metal ions (Fig. 1b). Although many polynuclear transition metal complexes of that kind are known for Co [8] and Cu [9], very few products resulting from OH hydrogen substitution in rhodoximes have been reported. Ramasami and Espenson [10] described the synthesis of $[ClRh(BF_2dmg)_2(PPh_3)]$, and Espenson and McHatton [11] showed that $[CH_3Rh\ (Hdmg)(H_2O)]$ reacts reversibly with $Fe(H_2O)_6^{3+}$ with the formation of the cation $[CH_3Rh(Hdmg)(Fedmg)\ (H_2O)]^{2+}$.

In a previous paper we described the synthesis of the tetranuclear bimetallic compound $[Rh(Hdmg)(ClZn\ dmg)(PPh_3)]_2$ featuring a Rh(II)–Rh(II) bond [12]. The interest in homo- and heterobimetallic complexes has recently increased, as the reactivity and properties of the

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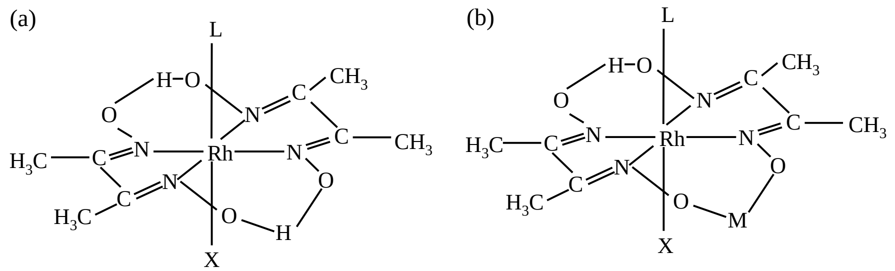


Fig. 1. (a) [Rh(Hdmg)$_2$XL] complexes, (b) [Rh(Hdmg)(Mdmg)XL].

metal core may be strongly modified by the presence of another metallic centre in close proximity. Two bonded or closely neighbouring non-bonded metal atoms may react with substrate molecules in a cooperative manner [13].

In this paper, based on the work we have carried out in this field, we report the synthesis and characterization of the first bimetallic complexes containing Rh(III) and Zn(II) centres, [Rh(Hdmg)(ClZndmg)(PPh$_3$)Cl] (**1a**) and its interesting ethanolic adduct [Rh(Hdmg){ClZn(C$_2$H$_5$OH)dmg}(PPh$_3$)Cl] (**1**). The complex salt [Rh(Hdmg)$_2$(PPh$_3$)$_2$]$^+$[Rh(Hdmg)$_2$(Cl)$_2$]$^-$ · 2CH$_3$OH (**2**) was isolated from the reaction mixture by treatment with the CHCl$_3$/CH$_3$OH solution. The simultaneous action of Zn/Hg and CH$_3$I on [Rh(Hdmg)(PPh$_3$)Cl] resulted in the compound [Rh(Hdmg)$_2$(PPh$_3$)I] · 0.5 C$_2$H$_5$OH (**3**). [Rh(Hdmg)$_2$(PPh$_3$)I] was obtained for the first time by Powell in a reaction of RhCl$_3$ · 3H$_2$O pretreated with KI before the addition of dimethylglyoxime and PPh$_3$ [7d], but was not characterized in detail then.

2. Experimental

2.1. Materials and measurements

RhCl$_3$ · 3H$_2$O was purchased from Pressure Chemical Co. All other chemicals were of reagent grade and were used in the commercially available form. UV–Vis spectra were monitored in the 200–820 nm range with a Hewlett Packard 8452A rapid scan diode array spectrometer. Infrared spectra were recorded on an FT-IR Nicolet Impact 400 spectrometer in the 4000–400 cm^{-1} range as KBr disks or Nujol mulls. The NMR spectra were measured on a Bruker AMX-300 spectrometer (^{1}H at 300.13 MHz, ^{31}P at 121.496 MHz) with TMS as internal standard and 85% H$_3$PO$_4$ as external standard for ^{1}H and ^{31}P{H}, respectively. Elemental analyses were performed at the Elemental Analysis Centre, Wrocław University, on a Perkin–Elmer Elemental Analyser 2400 for CHN.

2.2. Syntheses

All manipulations were performed under anaerobic conditions using standard Schlenk or vacuum line techniques unless stated otherwise. [Rh(Hdmg)$_2$(PPh$_3$)Cl] was prepared according to the procedure of Powell [7d].

The syntheses of compounds **1a**, **1**, **2**, and **3** followed the same initial procedure. A three-neck glass reactor equipped with a magnetic stirring bar, a reflux condenser connected to a mineral oil bubbler, a fritted glass inlet tube, and a dropping funnel was charged with [Rh(Hdmg)$_2$(PPh$_3$)Cl] (0.104 g, 0.16 mmol) and then deaerated in 10 vacuo/N$_2$ cycles. Subsequently 40 cm^3 of absolute ethanol (degassed) was added and the reaction mixture was heated at 55 °C until [Rh(Hdmg)$_2$(PPh$_3$)Cl] dissolved. Then the heating was stopped and Zn(Hg) beads (1%, 10 g) were added. After about 40 min of stirring a suspension of pink-yellow solid **A** in a brown-orange solution **B** was formed.

2.2.1. *[Rh(Hdmg)(ClZndmg)(PPh$_3$)Cl] (**1a**)*

After filtration, the solid **A**, contaminated with a reddish impurity, was further washed with a small amount of cold degassed dichloromethane and taken to dryness to give a pale yellow precipitate. Yield 47 mg, 40%. *Anal.* Calc. for C$_{26}$H$_{28}$N$_4$P$_1$O$_4$Cl$_2$ZnRh ($M = 730.66$): C, 42.74; H, 3.86; N, 7.70. Found: C, 42.84; H, 3.85; N, 7.60%. Selected IR frequencies (KBr), cm^{-1}: ν_{CN} 1564 (s), ν_{NO} 1234. NMR spectra (CDCl$_3$), ^{1}H: 15.64 (brs, O–H· · ·O), 7.43–7.28 (m, 15, P(C$_6$H$_5$)$_3$), 2.07 (s, 6, CH$_3$); 1.76 (s, 6, CH$_3$), ^{31}P{H}: 25.3 ppm (d, $^1J_{\mathrm{Rh–P}} = 122$ Hz).

2.2.2. *[Rh(Hdmg){ClZn(C$_2$H$_5$OH)dmg}(PPh$_3$)Cl] (**1**)*

Slow, multiple crystallization of **1a** from the CHCl$_3$/EtOH mixture led to red-gold, X-ray quality crystals of **1**. *Anal.* Calc. for C$_{28}$H$_{34}$N$_4$P$_1$O$_5$Cl$_2$ZnRh ($M = 776.73$): C, 43.29; H, 4.41; N, 7.21; P, 3.98. Found: C, 43.39; H, 4.38; N, 7.4; P, 3.89%. Selected IR absorption bands (KBr), cm^{-1}: ν_{CN} 1570 (s); ν_{NO} 1238 (vs). NMR spectra (CDCl$_3$), ^{1}H δ: 17.64 (brs, 1, OH), 13.3 (s, 1, OH), 7.43–7.28 (m, 15, P(C$_6$H$_5$)$_3$), 3.85 (qt, $J = 7.2$ Hz, 2, CH$_2$ (C$_2$H$_5$OH)); 1.96 (s, 6, CH$_3$); 1.91 (s, 6, CH$_3$), 1.28 ppm (t, $J = 7.2$ Hz, 3, CH$_3$ (C$_2$H$_5$OH)); ^{31}P{P}: 25.9 ppm (d, $^1J_{\mathrm{Rh–P}} = 125$ Hz).

2.2.3. $[Rh(Hdmg)_2(PPh_3)_2]^+[Rh(Hdmg)_2(Cl)_2]^- \cdot 2CH_3OH$ (**2**)

The filtrate **B** was evaporated under vacuum. Dissolution of the crude solid in $CHCl_3$ over time yielded a sandy solid, which was filtered off and dried in vacuo. Crystallization from CH_3OH gave pale yellow crystals of **2**. Yield 42 mg, 20%. *Anal.* Calc. for $C_{54}H_{66}N_8P_2O_{10}Cl_2Rh_2$ ($M = 1325.8$): C, 48.92; H, 5.02; N, 8.45. Found: C, 48.46; H, 5.23; N, 8.22%. Selected IR frequencies (KBr), cm^{-1}: ν_{CN} 1537 (s), ν_{NO} 1257 (vs). NMR spectra (CD_3OD), ^1H δ: 7.53–7.37 (m, 30, $P(C_6H_5)_3$), 2.31 (s, 12, CH_3 (Hdmg)), 1.34 ppm (brs, 12 (Hdmg)); ^{31}P: 18.51 ppm (d, $^1J_{Rh,P} = 90.17$ Hz). (CD_2Cl_2), ^1H: 7.31–7.18 (m, 30, $P(C_6H_5)_3$), 2.27 (s, 12, CH_3 (Hdmg)), 1.42 ppm (t, $^5J_{P,H} = 1.34$ Hz, 12 (Hdmg)); ^{31}P: 16.94 ppm (d, $^1J_{Rh,P} = 91$ Hz).

2.2.4. $[Rh(Hdmg)_2(PPh_3)I] \cdot 0.5C_2H_5OH$ (**3**)

On addition of CH_3I to the filtrate **B** the resulting mixture was stirred overnight at room temperature under nitrogen. The orange solution was evaporated to give a thick, syrupy liquid. This liquid was redissolved in a THF/EtOH mixture and left to stand in dark until brown-reddish micro-crystals appeared. They were collected by filtration, washed with ethanol, and dried in vacuo. Yield 24 mg, 20%. *Anal.* Calc. for $C_{27}H_{32}N_4PO_{4.5}IRh$ ($M = 745.36$): C, 43.51; H, 4.33; N, 7.52. Found: C, 43.51; H, 4.41; N, 7.74%. Selected IR absorption bands (KBr), cm^{-1}: ν_{CN} 1532 (w), ν_{NO} 1258 (s). NMR spectra ($CDCl_3$): ^1H, 7.48–7.36 (m, 15, PPh_3), 1.86 (s, 12, CH_3 (Hdmg)); ^{31}P: 16.34 ppm (d, $^1J_{Rh-P} = 112$ Hz).

2.3. X-ray structure determination

Crystal data are given in Table 1, together with refinement details. All measurements of crystals **1**, **2**, and **3** were performed on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. Crystals were positioned at 65 mm from the KM4CCD camera. 612 frames were measured at 0.75° intervals with a counting time of 15–30 s. The data were corrected for Lorentz and polarization effects. Absorption correction based on least-squares fitted against $|F_c| - |F_o|$ differences was applied for **1** and **3**. Data reduction and analysis were carried out using the Kuma Diffraction (Wrocław) programs [14]. The structure was solved by the heavy atom method (SHELXS 97 program [15]) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL 97 programs [16]. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were included from the geometry of molecules and $\Delta\rho$ maps; they were not refined for **1** and were refined with isotropic thermal parameters for **2** and **3**.

Table 1
Crystal and collection parameters for $[Rh(Hdmg)\{ClZn(C_2H_5OH)dmg\}(PPh_3)Cl]$ (**1**), $[Rh(Hdmg)_2(PPh_3)_2]^+[Rh(Hdmg)_2(Cl)_2]^- \cdot 2CH_3OH$ (**2**), and $[Rh(Hdmg)_2(PPh_3)I] \cdot 0.5C_2H_5OH$ (**3**)

	1	**2**	**3**
Empirical formula	$C_{28}H_{34}N_4PO_5Cl_2ZnRh$	$C_{54}H_{66}N_8P_2O_{10}$ Cl_2Rh_2	$C_{26}H_{29}N_4PO_4IRh \cdot 0.5C_2H_5OH \cdot$
Formula weight	776.74	1325.81	745.35
T (K)	200(1)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	10.946(2)	10.4681(9)	11.5142(9)
b (Å)	11.619(2)	10.6195 (11)	14.5389(10)
c (Å)	13.420(3)	14.7188(12)	16.8520(13)
α (°)	112.04(3)	91.051(7)	
β (°)	90.02(3)	100.431(7)	91.724(7)
γ (°)	93.19(3)	118.166(10)	
V (Å^3)	1579.2(5)	1408.4(2)	2819.8(4)
Z	2	1	4
D_c (Mg m^{-3})	1.634	1.563	1.756
μ (mm^{-1})	1.545	0.802	1.799
$F(000)$	788	680	1484
Crystal size (mm)	0.30 × 0.20 × 0.20	0.19 × 0.14 × 0.14	0.18 × 0.12 × 0.12
θ range for data collection (°)	3.39–28.75	3.45–28.47	3.51–28.70
Reflections collected	11,292	9788	19,833
Independent reflections (R_{int})	7161 (0.0208)	6189 (0.0282)	6715 (0.0308)
Data/parameters	7161/379	6180/488	6715/468
Absorption corrections min./max.	0.6543/0.7475		0.7378/0.8130
Goodness-of-fit (F^2)	1.039	1.070	1.099
Final R_1/wR_2 indices ($I > 2\sigma I$)	0.0346/0.0825	0.0260/0.0634	0.0471/0.1038
Largest differential peak/hole (e Å^{-3})	1.201/−0.750	0.752/−0.867	1.416/−1.940

3. Results and discussion

3.1. Synthesis and spectral characterization

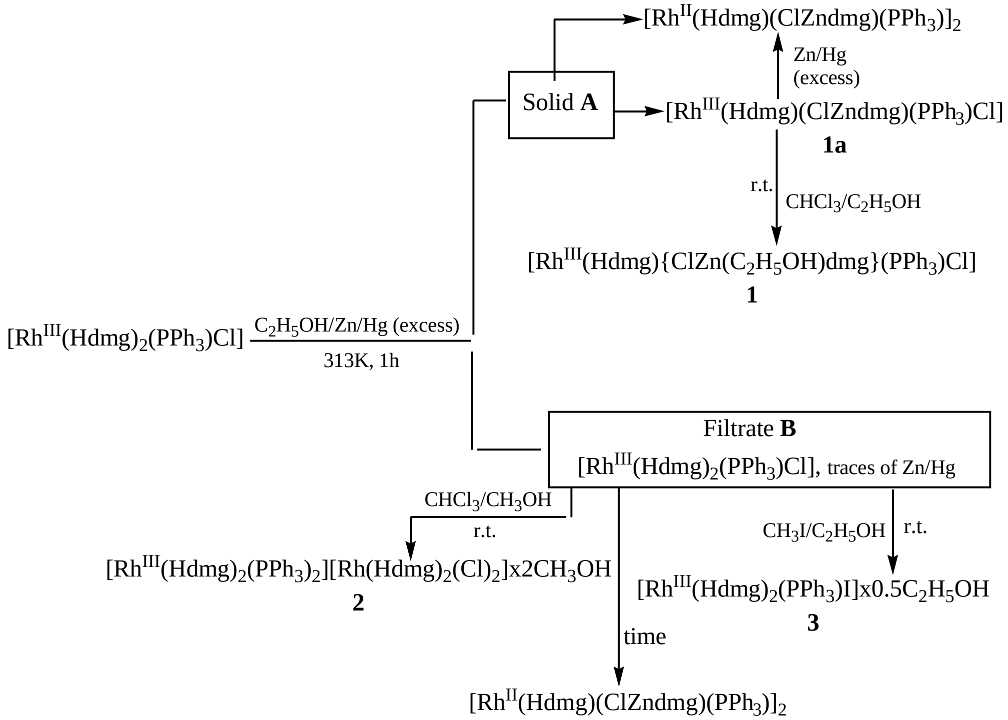
For the convenience of the reader the compounds and reactions are shown in Scheme 1.

A mixture of red and pale yellow precipitates (1:10) is formed during the first hour of the reaction of [Rh(Hdmg)$_2$(PPh$_3$)Cl] with zinc amalgam, carried out in C_2H_5OH. Based on the ^{1}H and ^{31}P{H} NMR spectra the red solid was found to be [Rh(Hdmg)(ClZndmg) (PPh$_3$)]$_2$ (^{1}H: 1.2, 1.4, 1.65, 1.72 ppm (CH$_3$ of dmg moieties); 7.2–7.6 ppm (PPh$_3$); ^{31}P: 3.6 ppm (vt, $J_{Rh,P} = 97$ Hz) [12]).

Combined NMR and elemental analysis data for the yellow species isolated from this mixture are consistent with the composition [Rh(Hdmg)(ClZndmg)(PPh$_3$)Cl] (**1a**). **1a**, containing a coordinatively unsaturated metal centre (Zn cation), seems to be an intermediate. The possibility to isolate this by-product and the subsequent formation of [Rh(Hdmg){ClZn(C$_2$H$_5$OH)dmg}(PPh$_3$) Cl] (**1**) upon repeated, slow crystallization from the CHCl$_3$/C$_2$H$_5$OH mixture may be accounted for by very low solubility of **1a** in ethanol. Unlike in **1a**, the presence of a molecule of ethanol in **1** is well evidenced by the ^{1}H NMR spectra. In the presence of an excess of Zn/Hg **1** and **1a** transform in time into [Rh(Hdmg)(ClZndmg) (PPh$_3$)]$_2$, being the final product with a yield of 60–70% [12].

The NMR spectra of the evaporated filtrate **B**, dissolved in CDCl$_3$, showed it to contain mainly unreacted [Rh(Hdmg)$_2$(PPh$_3$)Cl] and small amounts of both **1a** and [Rh(Hdmg)(ClZndmg)(PPh$_3$)]$_2$. The filtrate **B** also contained traces of finely dispersed Zn/Hg. **B** was found to react with CHCl$_3$ (CDCl$_3$) to form an inner salt [Rh(Hdmg)$_2$(PPh$_3$)$_2$]$^+$[Rh(Hdmg)$_2$(Cl)$_2$]$^-$ · 2CH$_3$OH (**2**). Although salts of this kind are well known for the related cobaloximes [17], only sparse data are available for rhodoximes [7a,7b,18,19]. The formation of the cobalt analogues has been found to be catalysed by Co(II) [17]. It is reasonable to suppose that the same mechanism can operate in the case of the presented reactions.

The reaction of the solution **B** with CH$_3$I, which afforded the compound [Rh(Hdmg)$_2$(PPh$_3$)I] · 0.5C$_2$H$_5$OH (**3**), seems to confirm the foregoing. The data presented here indicate that the interaction between [Rh(Hdmg)$_2$(PPh$_3$)Cl] and Zn/Hg not only produces the zinc substituted derivatives, but also unsubstituted Rh(II) units. The latter are well known to dimerize rapidly in the absence of other reagents [2g]. It appeared that the presence of organic as well as inorganic halides resulted in a conversion of the metal radical [Rh(Hdmg)$_2$PPh$_3$] to rhodium(III) halide abstraction compounds [2g,2h,20]. Thus it is possible that the same radical can effect the formation of **2**, which can stay in the equilibrium



Scheme 1.

$$2[\mathrm{Rh(Hdmg)_2(PPh)_3Cl}] \overset{\mathrm{Rh(II)}}{\rightleftharpoons} [\mathrm{Rh(Hdmg)_2(PPh_3)_2}][\mathrm{Rh(Hdmg)_2Cl_2}]$$

The interaction of the Rh(I) species, $[\mathrm{Rh(Hdmg)_2}]^-$, with alkylating agents leads to oxidative addition products – organorhodoximes [2,21].

The solution **B** left to stand alone, only in the presence of traces of Zn/Hg, affords over long time the dimer $[\mathrm{Rh(Hdmg)(ClZndmg)(PPh_3)}]_2$.

The ^{1}H resonances of the methyl protons for **1a** and **1** are registered as two singlets. This reflects the chemical inequivalence between the atoms of each dimethylglyoximato moiety due to the replacement of one of the hydrogen bonds by the $[\mathrm{ClZn}]^{1+}$ unit.

The shielding of the equatorial methyls was found to depend on the number of phosphine phenyls: no $\mathrm{PPh_3}$ (δ 2.31 ppm for the anion of **2**, 2.36 and 2.36–2.47 ppm for $[\mathrm{Rh(Hdmg)(H_2dmg)(Cl_2)}]$ and $[\mathrm{Rh(Hdmg)_2(H_2O)_2}](\mathrm{ClO_4})$, respectively [7a]); one $\mathrm{PPh_3}$ (δ 1.99 and 1.91 for **1**, 1.86 for **3** and 1.74–1.94 ppm for $[\mathrm{Rh(Hdmg)_2(PPh_3)Cl}]$ [7a,b]); two $\mathrm{PPh_3}$ (δ 1.34 for the cation of **2** and 1.38–1.48 for $[\mathrm{Rh(Hdmg)_2(PPh_3)_2}](\mathrm{ClO_4})$ [7a]). The singlet at 13.13 ppm in **1** originates from the OH proton of the bisdimethylglyoximato moiety. An identical value was observed for $[\mathrm{Rh(Hdmg)(ZnCldmg)(PPh_3)}]_2$ [12]. The proton of an OH group at 17.64 ppm in **1** is assigned to the ethanol molecule coordinated to zinc, forming the hydrogen bond with Cl bonded to Rh. In both cases, these signals were registered at room temperature. No OH proton signal was observed for **2** and **3**, which is in line with the finding that the protons of the O–H···O bridges could be observed for the rhodoximes containing the $\mathrm{(Hdmg)_2}$ unit at low temperature. At room temperature they undergo fast exchange with traces of water dissolved in the solvent [22].

The ^{31}P NMR spectra show one doublet for each of the compounds **1a** and **1**: δ 25.3 ($^1J_{\mathrm{Rh,P}} = 122$ Hz) and δ 25.9 ppm ($^1J_{\mathrm{Rh–P}} = 125$ Hz), respectively. Almost identical frequencies were registered for $[\mathrm{Rh(Hdmg)_2PPh_3Cl}]$ (23.8 ppm, 123 Hz) [6]. A doublet at 16.34 ppm with $^1J_{\mathrm{Rh–P}}$ of 112 Hz in **3** corroborates the X-ray data indicating that the *trans*-influence of I^- is slightly more pronounced than that of Cl^-. The $^1J_{\mathrm{Rh,P}}$ coupling constants of 90.17 and 91 Hz for the doublets at 18.51 and 16.7 ppm registered for **2** and $[\mathrm{Rh(Hdmg)_2(PPh_3)_2}](\mathrm{ClO_4})$ [6], respectively are consistent with the crystallographic data about the apical *trans*-influence.

3.2. *Crystal structures of* **1**, **2**, *and* **3**

Figs. 2 and 3 show the structures of the complexes $[\mathrm{Rh(Hdmg)\{CClZn(C_2H_5OH)dmg\}PPh_3Cl}]$ (**1**) and $[\mathrm{Rh(Hdmg)_2(PPh_3)_2}]^+[\mathrm{Rh(Hdmg)_2(Cl)_2}]^- \cdot 2\mathrm{CH_3OH}$ (**2**), respectively. The molecular structure of $[\mathrm{Rh(Hdmg)_2(PPh_3)I}] \cdot 0.5\ \mathrm{C_2H_5OH}$ (**3**) is depicted in Figs. 4 and 5. Selected bond lengths and angles are listed in Tables 2–4.

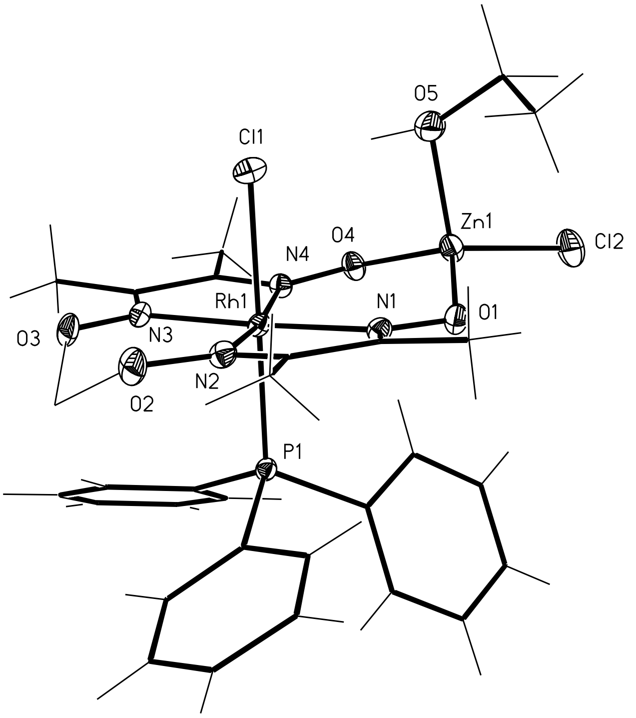


Fig. 2. Molecular structure of **1**.

The Rh atoms of all the investigated complexes display a distorted octahedral coordination, with the two dimethylglyoximate ligands in the equatorial plane and two other ligands in the axial positions. The average Rh–N separations are 2.014(2), 1.9942(6), 1.986(4) Å for **1**, **2**, and **3**, respectively and are comparable to those found for the complexes given in Table 5 [2a,7d,17,22]. The Rh–N distances are slightly longer in the cations than in the anions. The mean N–C distances of 1.294(4), 1.302(3), and 1.299(6) Å in **1**, **2**, and **3**, respectively are similar to those found for the complexes cited in Table 5 [2a,7c,18,23]. The Rh–P bond lengths deserve special attention. The Rh–P distance of 2.4245(5) Å in **2** is distinctly longer than those estimated for **1** and **3**, 2.3248(11) and 2.3441(11) Å, respectively. The latter values match the 2.327(1) Å bond length reported for $[\mathrm{Rh(Hdmg)_2(PPh_3)Cl}]$ [7c]. A comparison of the Rh–P lengths reveals mutual influence of the *trans*-coordinated $\mathrm{PPh_3}$ ligands, also demonstrated by the $J_{\mathrm{Rh,P}}$ couple constants in ^{31}P NMR spectra, vide supra.

The Rh–X axial separations 2.4022(12), 2.3317(5) (X = Cl for **1** and **2**), and 2.6879(5) Å, (X = I for **3**) follow the trend of covalent radii, Cl<I and are in line with those found for [Rh(Hdmg)pyCl], 2.3290(4) Å, and for [Rh(Hdmg)pyI], 2.6423(4) Å [2a].

A significant change for H-bonded Hdmg rings was registered for **1**. The distance between O(2) and O(3), 2.471(3) Å, in **1** is distinctly shorter than the distance of 2.664(6) Å (average) estimated for the O···O contacts in

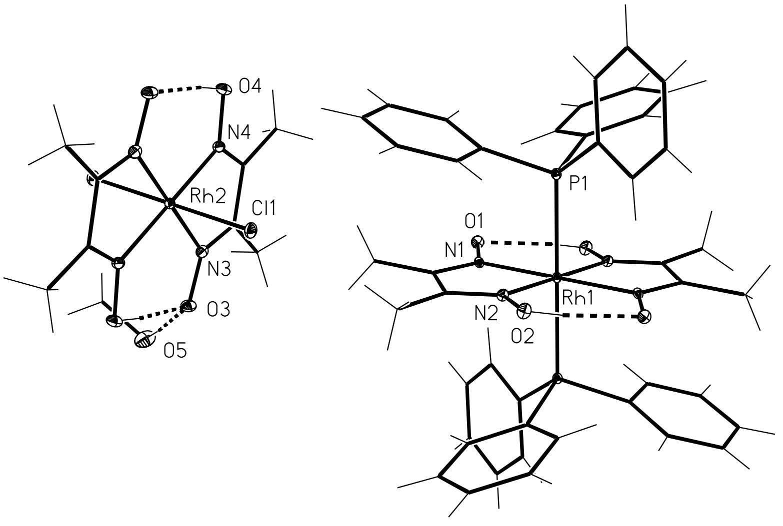


Fig. 3. Molecular structure of **2**.

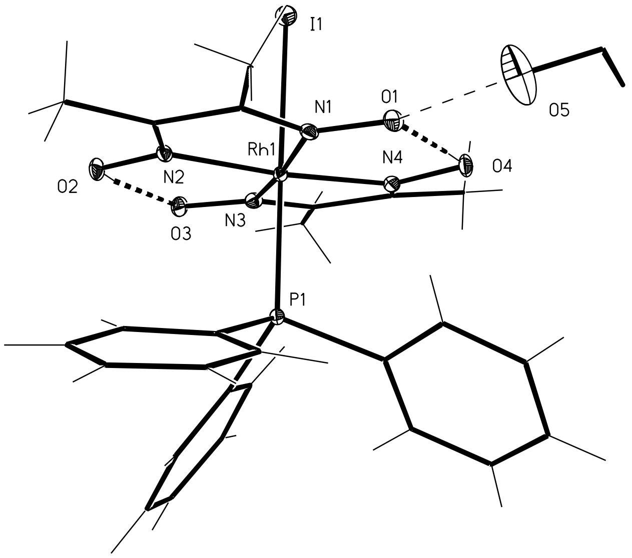


Fig. 4. Molecular structure of **3**.

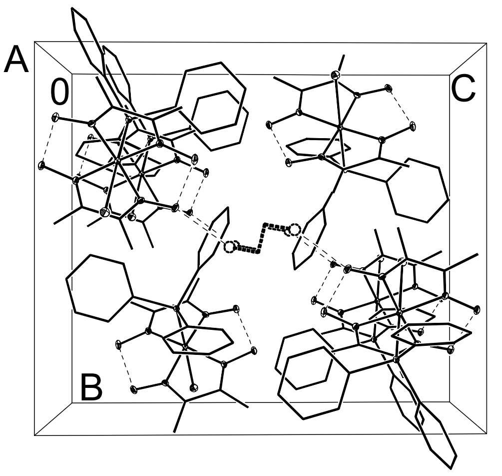


Fig. 5. Packing diagram of complex **3** viewed along the *c*-axis of the unit cell. Disordered (1:1) molecules of ethanol are represented by the heavy dashed lines. The remaining dashed lines represent the O–H···O hydrogen bonds.

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

Bond distances			
Rh(1)–N(2)	1.994(2)	O(1)–N(1)	1.339(3)
Rh(1)–N(3)	1.996(2)	O(2)–N(2)	1.343(3)
Rh(1)–N(1)	2.031(2)	O(3)–N(3)	1.339(3)
Rh(1)–N(4)	2.035(2)	O(4)–N(4)	1.345(3)
Rh(1)–P(1)	2.3248(11)	O(5)–C(9)	1.458(5)
Rh(1)–Cl(1)	2.4022(12)	N(1)–C(2)	1.301(3)
Zn(1)–O(1)	1.937(2)	N(2)–C(3)	1.283(4)
Zn(1)–O(4)	1.946(2)	N(3)–C(6)	1.295(4)
Zn(1)–O(5)	2.056(2)	N(4)–C(7)	1.295(4)
Zn(1)–Cl(2)	2.1847(11)		
Bond angles			
N(2)–Rh(1)–N(3)	96.89(10)	N(2)–Rh(1)–N(4)	172.60(9)
N(2)–Rh(1)–N(1)	77.73(10)	N(3)–Rh(1)–N(4)	77.96(10)
N(3)–Rh(1)–N(1)	173.47(9)	N(1)–Rh(1)–N(4)	107.04(10)
P(1)–Rh(1)–Cl(1)	179.51(3)		

Table 3
Selected distances (Å) and angles (°) for **2**

Bond distances			
Rh1–N1	2.0196(16)	O1–N1	1.304(2)
Rh1–N2	1.9842(16)	O2–N2	1.376(2)
Rh1–P1	2.4245(5)	O3–N3	1.323(2)
Rh2–N3	1.9930(17)	O4–N4	1.370(2)
Rh2–N4	1.9805(17)	N2–C3	1.297(2)
Rh2–Cl1	2.3317(5)	N3–C24	1.306(3)
N1–C2	1.313(2)	N4–C25	1.293(3)
Bond angles			
$N2^i$–Rh1–N2	180.0	N4–Rh2–$N4^{ii}$	180.0
$N2^i$–Rh1–$N1^i$	78.00(6)	N4–Rh2–N3	78.86(7)
$N2^i$–Rh1–$N1^i$	102.00(6)	$N4^{ii}$–Rh2–N3	101.14(7)
P1–Rh1–$P1^i$	180.0	$Cl1^{ii}$–Rh2–Cl1	180.0

Symmetry transformations used to generate equivalent atoms: none x, y, z; (i) $-x, 1-y, 1-z$; (ii) $2-x, -y, -z$.

Table 4
Selected distances (Å) and angles (°) for **3**

Bond distances			
Rh(1)–N(2)	1.973(4)	O(2)–N(2)	1.372(5)
Rh(1)–N(4)	1.985(4)	O(3)–N(3)	1.318(5)
Rh(1)–N(3)	1.989(4)	O(4)–N(4)	1.377(5)
Rh(1)–N(1)	1.996(4)	N(1)–C(2)	1.297(6)
Rh(1)–P(1)	2.3441(11)	N(2)–C(3)	1.295(6)
Rh(1)–I(1)	2.6879(5)	N(3)–C(6)	1.310(6)
O(1)–N(1)	1.315(5)	N(4)–C(7)	1.295(6)
Bond angles			
N(2)–Rh(1)–N(4)	174.91(15)	N(3)–Rh(1)–P(1)	94.59(11)
N(2)–Rh(1)–N(3)	100.29(15)	N(1)–Rh(1)–P(1)	91.12(11)
N(4)–Rh(1)–N(3)	78.81(15)	N(2)–Rh(1)–I(1)	89.08(10)
N(2)–Rh(1)–N(1)	78.78(15)	N(4)–Rh(1)–I(1)	85.87(10)
N(4)–Rh(1)–N(1)	101.60(15)	N(3)–Rh(1)–I(1)	86.53(10)
N(3)–Rh(1)–N(1)	174.23(15)	N(1)–Rh(1)–I(1)	87.76(10)
N(2)–Rh(1)–P(1)	91.01(11)	P(1)–Rh(1)–I(1)	178.84(3)

Table 5
Selected bond lengths in rhodoximes (Å)

Compound	Rh–N (av)	N–O (av)	N–C (av)	Rh–L		Reference
$[Rh(Hdmg)(ClZn\{C_2H_5OH\}dmg)\ (PPh_3)Cl]$ (**1**)	2.014(2)	1.342(3)	1.294(4)	2.4022(12), 2.3248(11),	Rh–Cl, Rh–P	this work
$[Rh(Hdmg)_2(PPh_3)_2]^+$	2.0019(16)	1.340(2)	1.305(2)	2.4245(5),	Rh–P	this work
$[Rh(Hdmg)_2(Cl_2)] \cdot 2CH_3OH^-$ (**2**)	1.9865(17)	1.3447(2)	1.299(3)	2.3317(5),	Rh–Cl	
$[Rh(Hdmg)_2(PPh_3)I] \cdot 0.5EtOH$ (**3**)	1.986(4)	1.346(5)	1.299(6)	2.6879(5), 2.3441(11),	Rh–I Rh–P	this work
$[Rh(Hdmg)((H_2dmg)Cl_2]$	1.997(10)	1.349(13)	1.301(15)	2.322(3)	Rh–Cl	[23]
$[Rh(Hdmg)_2)(NH_3)_2]^+$	1.998(5)	1.345(6)	1.302(6)	2.078(6),	Rh–NH_3	[18]
$[Rh(Hdmg)Cl_2]^-$	1.990(5)	1.350(5)	1.291(7)	2.329(1),	Rh–Cl	
$[Rh(Hdmg)_2(PPh_3)Cl]$	1.992(4)	1.337(6)	1.296(7)	2.381(1), 2.327(1),	Rh–Cl Rh–P	[7c]
$[Rh(Hdmg)_2pyI]$				2.6423(4) 2.079(3)	Rh–I Rh–py	[2a]
$[Rh(Hdmg)_2\ pyCl]$				2.3290(4)	Rh–Cl	[2a]

the $[Rh(Hdmg)(PPh_3)Cl]$ complex [7c]. The distance of 3.260(3) Å between the zinc-chelating oxygen atoms, O(1)–O(4), is almost identical to that found for $[Rh(Hdmg)(ClZndmg)(PPh_3)]_2$, 3.25 Å [12]. An interesting feature is that the zinc cation of **1** binds two oxygen atoms of the dmg^{2-} moiety at the mean distance of 1.9415(2) Å, the Cl^- anion at 2.4022(12) Å, and additionally one ethanol molecule through the O(5) oxygen at a distance of 2.056(2) Å, thus forming a tetrahedral environment of the Zn^{2+} cation (Table 2). At the same time the same ethanol molecule forms the OH···Cl–Rh hydrogen bond with a distance of 3.072(3) Å.

The O···O contacts between the dimethylglyoxime rings in **2** are 2.728(2) and 2.695(2) Å for the cation and anion, respectively. The methanol molecule is bonded to the O(5)–H···O(3) moiety at a distance of 2.763(2) Å. The distances O(4)···O(1) and O(2)···O(3), 2.716(5) and 2.600(5) Å, respectively, for **3**, are in the range for O atoms in O–H···O bridges.

To sum up, the first instance of a bimetallic oximato compound containing Rh(III) and Zn(II) centres, **1**, has been obtained and structurally determined in addition to two new rhodoximes, **2** and **3**. It has been demonstrated that rhodium compounds with dioximato ligands can serve as suitable models for designing heteronuclear complexes. Our investigations have shown the ability of the coordination sphere in rhodoximes to undergo many different rearrangements, which can influence the activity of the rhodium centre.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. CCDC –199485, 199486 and 199487 for structures **1**, **2** and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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