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Rhodium complexes with diacetyl monoxime ligands; crystal structure of [Rh*cis*-$(C_4H_6NO)_2$*cis*-$(PPh_3)_2]ClO_4 \cdot CHCl_3$

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Abstract—The reaction of $RhCl_3 \cdot 3H_2O$ with Hdamo and PPh_3 (Hdamo = diacetyl monoxime = C_4H_7NO), both in the absence (**1**) and in the presence of $HClO_4$ (**2**) afforded the complex $Rh(damo)(PPh_3)_2Cl_2$. The reaction of the acidic water/ethanolic solution of $[Rh(H_2O)_6]^{3+}$ with Hdamo and PPh_3 (**3**) gave the mixture of the isomers of the compound $[Rh(damo)_2(PPh_3)_2]ClO_4$ (**3A** and **3B**). A similar mixture of isomers was formed when $[Rh(H_2O)_6]^{3+}$ reacted with H_2dopn (H_2dopn = 3,9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioxime) and PPh_3 (**4**). Two isomers (**4A** = **3B**) and [Rh*cis*-$(damo)_2$*cis*-$(PPh_3)_2]ClO_4 \cdot CHCl_3$ (**4B**) have been isolated. All the compounds were characterized by elemental analysis NMR and IR spectroscopy. Single-crystal X-ray diffraction studies were carried out on the complex **4B**. In this compound the coordination environment around rhodium(III) is pseudooctahedral composed of two *cis*-oxime nitrogen atoms [av. Rh—N = 2.031(3) Å], two *trans*-oxime oxygen atoms [av. Rh—O = 2.026(2) Å] and two *cis*-phosphine phosphorus atoms [av. Rh—P = 2.403(1) Å]. Copyright © 1996 Elsevier Science Ltd

Keywords: rhodium complexes; rhodoxime complexes; monoxime complexes; crystal structure.

Until recently the chemistry of rhodium compounds with bidentate oximato ligands was by and large limited to the presence of two dioximato groups, coordinated to a metal center through four nitrogen atoms. For these substances ligands in the equatorial plane are equivalent and perturbations were largely the result of varying the axial ligands or the nature of the R group of the dioximato ligands [1–6].

There are no reports of rhodium complexes containing monoximato ligands (Fig. 1) with donor atoms other than nitrogen. An exception is the complex of rhodium(III) with the 3-methoxy-3-methyl-2-butanone oxime [7]. The starting material used for syntheses of most rhodium compounds with dioximes is $RhCl_3 \cdot 3H_2O$. Very recently studies on a reaction between $[Rh(H_2O_6]^{3+}$, H_2dmg (H_2dmg = dimethylglyoxime) and $[Rh(H_2O)_6]^{3+}$, H_2dmg and PPh_3 resulted in isolation of complexes $[Rh(dmgH)_2(L)_2]ClO_4$, (L = H_2O, PPh_3) [8], which are impossible to obtain in syntheses using the former starting material. This prompted us to carry out the reactions in a few different systems:

(1) $RhCl_3 \cdot 3H_2O + Hdamo + PPh_3 \rightarrow Rh(damo)(PPh_3)_2Cl_2$
(2) $RhCl_3 \cdot 3H_2O + Hdamo + PPh_3/HClO_4 \rightarrow Rh(damo)(PPh_3)_2Cl_2$
(3) $[Rh(H_2O)_6]^{3+} + Hdamo + PPh_3/HClO_4 \rightarrow [Rh(damo)_2(PPh_3)_2]ClO_4$
3A and/or **3B**
(4) $[Rh(H_2O)_6]^{3+} + H_2dopn + PPh_3/HClO_4 \rightarrow [Rh(damo)_2(PPh_3)_2]ClO_4$
4A and/or **4B**

The complex containing one damo$^-$ anion $[Rh(damo)(PPh_3)_2Cl_2]$ has been found as the product of the reactions (**1**) and (**2**) whereas three isomeric forms of the compound $[Rh(damo)_2(PPh_3)_2]ClO_4$ with two coordinated damo$^-$ ions have been identified as the

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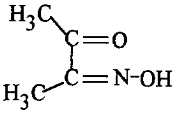

Hdamo

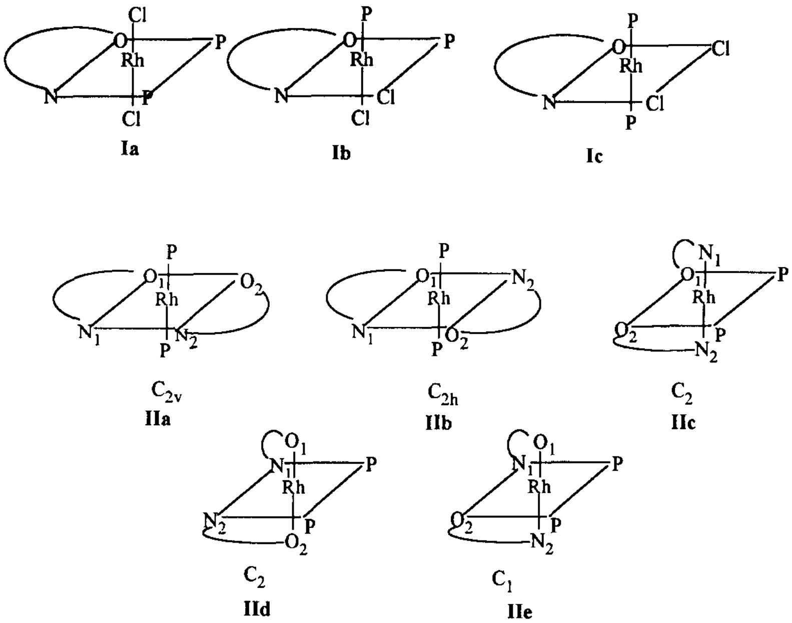

Fig. 1. Possible substitution products for compounds of general formula (I) Rh(damo)L_2Cl_2 and (II) [Rh(damo)$_2L_2$]ClO_4, (L = PPh_3 = P).

products of the reactions (**3**) and (**4**). Complexes containing mixed hetero donor atoms in the basal plane are far more complex with respect to their electronic and/or structural effects than rhodium dioximates. The effect of such changes is bound to reflect on the electronic structure of the rhodium center as well as on potential chemistry that may occur in the axial and/or equatorial direction of a given isomer.

As seen in Fig. 1, there are few possible geometrical isomers for compounds of general formula [Rh (damo)L_2Cl_2] (L = PPh_3) and [Rh(damo)$_2L_2$]ClO_4, (L = PPh_3) for five-membered N,O-chelation which is common for most metal complexes with oximes, although six-membered O,O-chelation cannot be excluded [9].

As far as we are aware complexes presented in this paper are the first examples of rhodium compounds containing diacetyl monoximato ligands.

EXPERIMENTAL

Physical measurements

UV–vis spectra were monitored on a Hewlett-Packard 8452A rapid scan dioda-array spectrometer. The NMR spectra were recorded on a Bruker spectrometer (^1H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.496 MHz) with solvent signals being used as internal standards for ^1H and ^{13}C, and external 85% H_3PO_4 for ^{31}P. Infrared spectra were measured in the range 4000–400 cm^{-1} as KBr disks on a Nicolet FTIR spectrophotometer.

Materials

$RhCl_3 \cdot H_2O$ was purchased from Aldrich. The compound [$Rh(H_2O)_6$]ClO_4 was synthetized according to the method of Ayres and Forrester in the reaction of $RhCl_3 \cdot 3H_2O$ with concentrated perchloric acid. Solutions were standardized spectrophotometrically by using the known absorption spectrum of [$Rh(H_2O)_6$]$^{3+}$, with peaks at 311 (ε = 67.4 M^{-1} cm^{-1}) and 396 nm (ε = 62) [10]. H_2Dopn was prepared by literature method [11]. All other chemicals were of reagent grade and were used as commercially obtained.

CAUTION! Perchlorate salts of metal complexes are potentially explosive. Only a small amount of material should be prepared, and it should be handled with caution.

Synthesis of Rh(damo)$(PPh_3)_2Cl_2$ (*Reaction* **1**). Hdamo ligand (0.082 g, 0.81 mmol) dissolved in 10 cm^3 of hot ethanol was combined with $RhCl_3 \cdot 3H_2O$ (0.104, 0.4 mmol) in 3 cm^3 of warm ethanol. The solution was refluxed for 5 min. PPh_3 (0.209 g, 0.8 mmol) dissolved in 10 cm^3 of hot EtOH was next added and the solution was heated under reflux for 15 min. The initial red colour of the solution turned to dark yellow, and was filtered while hot. Upon standing at ambient temperature, the mixture deposited the yellow microcrystalline product which was filtered off, washed with small portions of ethanol, diethyl ether, and air-dried. Yield: 0.25 g (79%). Found: C, 60.0; H, 4.3; N, 1.7. Calc. for $RhC_{40}H_{36}N_1P_2O_2Cl_2$: C 60.2; H, 4.5; N, 1.7%. NMR spectra ($CDCl_3$), δ (ppm): ^{1}H: 1.054(s) ($\mathrm{C}H_3$(CO)) (3H), 1.42(s) ($\mathrm{C}H_3$(CN)) (3H), 7.28–7.75(m) aromatic (30H); ^{31}P: 18.56(d), ^1J(Rh,P) = 91.9 Hz.

Reaction **2**. A hot ethanolic solution (10 cm^3) of Hdamo (0.083 g, 0.82 mmol) was added to a 3 mol dm^{-3} $HClO_4$ solution in water (10 cm^3) containing $RhCl_3 \cdot 3H_2O$ (0.104, 0.4 mmol). The resulting solution was kept under reflux for 2 h. PPh_3 (0.215 g, 0.82 mmol) dissolved in 20 cm^3 of hot ethanol was added to the reaction mixture. After 1 h heating the solution was filtered and left to stand at room temperature. The yellow microcrystalline product was filtered off, washed with ethanol, diethyl ether and air-dried. Yield: 0.18 g (57%). Found: C, 59.9; H, 4.43; N, 1.70. Calc. for $RhC_{40}H_{36}N_1P_2O_2Cl_2$: C, 60.2; H, 4.5; N, 1.7%. NMR spectra ($CDCl_3$), δ (ppm): ^{1}H: 1.054(s) ($\mathrm{C}H_3$(CO)) (3H), 1.42(s) ($\mathrm{C}H_3$(CN)) (3H), 7.28–7.75(m) aromatic (30H); ^{31}P: 18.55(d) ^1J(Rh—P) = 91.9 Hz; ^{13}C: 12.36 ($C\mathrm{H}_3$(C—N)), 23.05 ($C\mathrm{H}_3$(CO)), 128.43 (P(m-$C_6H_5)_3$), 129.14(vt) (P(i-$C_6H_5)_3$), 131.02 (P(p-$C_6H_5)_3$), 135.67(P(o-$C_6H_5)_3$), 152.26 (C—N), 200.27 (C—O). No IR bands due to the ClO_4^- anion were detected.

Synthesis of $[Rh(damo)_2(PPh_3)_2]ClO_4$ (*Reaction* **3**). To a solution of $[Rh(H_2O)_6]^{3+}$ (1.02 mmol) in 3 mol dm^{-3} $HClO_4$, Hdamo (0.204 g, 2.04 mmol) in 15 cm^3 of hot ethanol was added and the resulting mixture refluxed for 2 h. PPh_3 (0.46 g, 2.04 mmol) dissolved in 20 cm^3 of hot EtOH was added and reaction mixture heated under reflux for 20 min. After filtration while hot the solution was cooled to room temperature. The product crystallized out as pale yellow microcrystals, which were filtered off, washed with ethanol and diethyl ether and air-dried. Yield: 0.37 g (40%). Found: C, 56.9; H, 4.4; N, 3.0. Calc. for $RhC_{44}H_{42}N_2P_2O_8Cl$: C, 57.0, H, 4.6; N, 3.0%. IR (as KBr pallets): medium band at 623 cm^{-1} due to $\nu(ClO_4^-)$. NMR spectra of the isolated precipitate indicated two components: **3A** and **3B**.

3A. NMR spectra, δ (pm): ^{1}H ($CDCl_3$) 0.92 s ($\mathrm{C}H_3$(CO)) (6H), 1.59 s ($\mathrm{C}H_3$(CN)) (6H), 7.4–7.59 (aromatic) (30H); (CD_2Cl_2): 0.88 s (6H), 1.55 s (6H), 7.57–7.49 m (30H), ^{31}P ($CDCl_3$): 21.2 d ^1J(Rh,P) = 97.2 Hz; (CD_2Cl_2): 21.42 ^{1}J(Rh,P) = 97.6 Hz, ^{13}C (CD_2Cl_2): 11.63 ($C\mathrm{H}_3$(CN)), 23.82 ($C\mathrm{H}_3$(CO), 125.6 d (P(i-$C_6H_5)_3$), 129.1 vt (P(m-C_6H_5), 132.4 s (P(p-C_6H_5), 134.6 vt (P(o-$C_6H_5)_3$), 157.4 (C—N), 204. (C—O).

3B. NMR spectra, δ (ppm): ^{1}H ($CDCl_3$): 0.96 s ($\mathrm{C}H_3$(CO)) (6H), 1.55 s ($\mathrm{C}H_3$(CN)) (6H), 7.37–7.48 m (aromatic) (30H), (CD_2Cl_2): 0.93 s (6H), 1.48 s (6H), 7.38–7.55 (m) (30H), ^{31}P ($CDCl_3$): 20.62 d ^1J(Rh,P) = 92.9 Hz; (CD_2Cl_2): 20.82 d ^1J(Rh,P) = 92.9 Hz, ^{13}C (CD_2Cl_2): 10.71 ($C\mathrm{H}_3$(CN)), 23.3 ($C\mathrm{H}_3$(CO), 125 d (P(i-$C_6H_5)_3$), 129.1 vt (P(m-C_6H_5), 132.4 s (P(p-C_6H_5), 134.3 vt (P(o-$C_6H_5)_3$), 153.1 (C—N), 202.7 (C—O).

Reaction **4**. The solution of $[Rh(H_2O)_6]^{3+}$ (1.1 mmol) in 3 mol dm^{-3} $HClO_4$ was combined with the hot ethanolic solution in H_2Dopn (0.227 g, 1.2 mmol). The solution was refluxed for 2 h; during this time a brown–yellow solution with a concomitant formation of a white solid resulted. After reduction of the solution volume down to 3–5 cm^3, the white precipitate was filtered off, washed with a small amount of ethanol, ethyl ether and air dried. Yield: 0.285 g (90%). Found: C, 13.3; H, 4.5; N, 10.2. Calc. for $C_3H_{12}N_2O_8Cl_2$: C, 13.1; H, 4.4; N, 10.2%. IR (as KBr disk): 629 cm^{-1} due to ν (ClO_4^-). NMR spectra (D_2O): ^{1}H: 2.11 CH_2 (2), 3.15 CH_2 (4). The clear brown–yellow filtrate was next charged with 0.61 g (2.3 mmol) of PPh_3 dissolved in warm ethanol. After 1 h of heating the solution was cooled to room temperature. The brownish–golden precipitate (**4A**) deposited as a first crop was filtered off, washed with ethanol, diethyl ether and air-dried. Yield: 0.31 g (30%). Found: C, 57.0; H, 4.6; N, 2.9. Calc. for $RhC_{44}H_{42}N_2P_2O_8Cl$: C, 57.0; H, 4.6; N, 3.0%. IR (as KBr disc): 625 cm^{-1}, ν (ClO_4^-). NMR spectra, δ (ppm): ^{1}H ($CDCl_3$): 0.96 s ($\mathrm{C}H_3$(CO)) (6H), 1.55 s ($\mathrm{C}H_3$(CN)) (6H), 7.4–7.6 m (aromatic) (30H); (CD_2Cl_2): 0.93 s (6H), 1.48 s (6H), 7.38–7.55 m (30H): (dmso-d_6): 0.89 s (6H), 1.57 s (6H), 7.3–7.65 m (30H); ^{31}P ($CDCl_3$): 20.6 d ^1J(Rh,P) = 93 Hz); (CD_2Cl_2): 20.8 d ^1J(Rh,P) = 93 Hz; ^{13}C (CD_2Cl_2): 10.81 ($C\mathrm{H}_3$(C—N)), 23.34 ($C\mathrm{H}_3$(C—O)), 125.23 (vt) (P(i-$C_6H_5)_3$), 129.22 vt (P(m-C_6H_5), 132.52 s (P(p-C_6H_5), 134.69 vt (P(o-$C_6H_5)_3$), 157.5 (C—N), 204.1 (C—O).

When the solution was allowed to stand overnight, the second crop **4B** crystallized out as the yellow microcrystals, which after filtration and washing with ethanol and diethyl ether were air-dried. Dark yellow single crystals [Rh*cis*-$(damo)_2$*cis*-$(PPh_3)_2]ClO_4 \cdot CHCl_3$ were obtained by slow evaporation in a refrigerator from a $CHCl_3$/EtOH solution of the crop **4B**. Yield: 0.25 g (25%). Found: C, 51.4; H, 4.2; N, 2.6. Calc. for $RhC_{45}H_{43}N_2P_2O_8Cl_4$: C, 51.6; H, 4.1; N, 2.7%. IR (as KBr disc): 625 cm^{-1}, ν (ClO_4^-). NMR spectra ($CDCl_3$), δ (ppm): ^{1}H: 1.33 s ($\mathrm{C}H_3$(CO)) (6H), 2.36 s ($\mathrm{C}H_3$(CN)) (6H), 7.3–7.5 (m) aromatic (30H); ^{31}P: 17.2 d ^1J(Rh,P) = 103.9 Hz; ^{13}C: 12.16 ($C\mathrm{H}_3$(C—N)), 26.05 ($C\mathrm{H}_3$(C—O)), 125.65 vt, (P(i-$C_6H_5)_3$), 129.4 (P(m-$C_6H_5)_3$), 132.2 (P(p-$C_6H_5)_3$), 134.6 (P(o-$C_6H_5)_3$), 153.2 (C—N), 209.83 (C—O).

X-ray diffraction

Preliminary examination of the crystal of [Rh*cis*-$(damo)_2$*cis*-$(PPh_3)_2]ClO_4 \cdot CHCl_3$ by Weissenberg photographs indicated the triclinic system. Data were collected on a Kuma KM-4 κ-axis diffractometer with graphite-monochromated Mo-K_α radiation using the ω-2θ scan mode. 6427 independent reflections measured were observed ($F > 4\sigma(F)$). Three standard reflections showed no variation. Data were corrected for Lorentz and polarization effects. Experimental details are given in Table 1. The structure was solved using SHELXS-86 [12] and refined by full-matrix least-square methods using SHELXL-93 [13] with anisotropic thermal parameters for non-H atoms. In the final cycles of the refinement H-atom parameters were included. Scattering factors were those incorporated in the SHELXL-93 program.

RESULTS AND DISCUSSION

X-ray studies of [Rhcis-(damo)$_2$cis-(PPh$_3$)$_2$]ClO$_4\cdot$CHCl$_3$

The crystal structure consists of [Rh(damo)$_2$(PPh$_3$)$_2$]$^+$ cations, ClO$_4^-$ anions and solvate CHCl$_3$ molecules, held together by electrostatic and van der Waals interactions, Fig. 2. Bond lengths and angles are given in Tables 2 and 3, respectively. The complex cations contain a pseudooctahedral arrangement of two PPh$_3$ ligands *cis-* to each other, and two bidentate damo$^-$ anions. The latter coordinate to the rhodium(III) ions in a chelating fashion through the oxime nitrogens and carbonyl oxygen atoms, forming five membered rings which remain planar. The complex cations have nearly C$_2$ symmetry. The rhodium atom is displaced out of the plane defined by two *cis*-oxime nitrogen and two *cis*-phosphorus atoms of PPh$_3$ by 0.0107(3) Å towards the O(4) oxime atom. The P(1)-Rh-P(2) angle, 98.42(4)°, is somewhat greater than the ideal angle of 90°. The angles: O(2)—Rh—O(4), 168.8(1)°, N(1)—Rh—P(1), 172.8(1)° and N(2)—Rh—P(2), 171.96(9)° are not strictly *trans*. This decrease is attributable to the presence of two bulky PPh$_3$ ligands in the *cis* position. The bite angles of the two chelates: O(2)—Rh—N(1) and O(4)—Rh—N(2) are similar, 78.7(1) and 79.1(1)° respectively. The Rh—P bonds, 2.401(1) and 2.406(1) Å, are slightly shorter than 2.447(1) in [Rh(dmgH)$_2$(PPh$_3$)(C$_2$H$_3$)] [17] and 2.461(2) Å in [Rh(dmgH)$_2$(PPh$_3$)(C$_2$H$_5$)] [18] but longer than 2.327(1) Å in Rh(dmgH)$_2$(PPh$_3$)Cl [19]. The average Rh—N distance 2.031(3) Å is long compared to the known rhodium(III) complexes containing the dmgH ligands in the equatorial plane, as well as to the compound of formula [Rh(ether oxime)$_2$Cl$_2$] [7]. In Rh(dmgH)$_2$(PPh$_3$)Cl, [Rh(dmgH)$_2$(PPh$_3$)(C$_2$H$_3$)], [Rh(dmgH)$_2$(PPh$_3$)(C$_2$H$_5$)] and [Rh(ether oxime)$_2$Cl$_2$], the average Rh—N bond lengths are 1.992(4), 1.957(2), 1.948(6) and 1.958(3) Å, respectively. The torsion angles N(1)—C(1)—C(2)—O(2) and N(2)—C(5)—C(6)—O(4) are 2.40(5) and 2.08(5)° respectively. The dihedral angle between these planes is 109.5(5)°. The N—C—C—O planes are perpendicular to the N(1)N(2)P(1)P(2) coordination plane. The rhodium atom is displaced 0.252(3) Å from the N(1)C(1)C(2)O(2) plane, and 0.197(3) Å from the N(2)C(5)C(6)O(4) plane. The O(1) and O(3) atoms are displaced 0.043(3) Å and −0.043(3) Å, respectively from these damo planes. The C(1)—C(2) and C(5)—C(6) bond lengths average 1.407(5) Å, and are in good agreement with a C(sp^2)—C(sp^2) double bond value for carbon in trigonal hybridization. As far as the carbon–oxygen and nitrogen–oxygen bonds are concerned, the average values 1.270(4) Å and 1.247(4) Å respectively, reveal a significant percentage of double-bond character in both ligands. Finally the carbon–nitrogen bond, 1.337(5) Å is in good agreement with single bond values. Of special note is the mutual position of rings C$_{21}$—C$_{26}$ and C$_{41}$—O$_{46}$ bound to the two different phosphorus atoms of the PPh$_3$ ligands, P$_1$ and P$_2$, respectively. The angle between these planes is 3.5°, indicating them to be almost parallel.

Table 1. Crystal data and structure refinement

Empirical formula	C$_{45}$H$_{42}$C$_{14}$N$_2$O$_8$P$_2$Rh
Formula weight	1045.46
Crystal size (mm)	0.07 × 0.09 × 0.15
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.402(2)
b (Å)	13.109(3)
c (Å)	16.191(3)
α (°)	91.83(3)
β (°)	102.26(3)
γ (°)	95.71(3)
V (Å^3)	2349.6(8)
Z	2
Density (calculated) (mg m^3)	1.478
Density (measured) (mg m^3)	1.48
Absorption coefficient (mm^{-1})	0.712
F(000)	1066
Theta range (°)	2.00 to 25.00
Scan ranges:	$0 \leqslant h \leqslant 13$, $-15 \leqslant k \leqslant 15$, $-19 \leqslant l \leqslant 18$
Measured reflections	6427
Independent reflections	6427
Data/restraints/parameters	6427/0/559
Goodness-of-fit	1.088
R	0.0350
wR	0.1013
Largest diff. peak and hold	0.613 and −0.582 e Å^{-3}

Studies of reactions

Reactions **1** *and* **2**. Reaction of RhCl$_3\cdot$3H$_2$O with Hdamo (**1**) gave the yellow product of formula [Rh(damo)(PPh$_3$)$_2$Cl$_2$]. The same compound was obtained

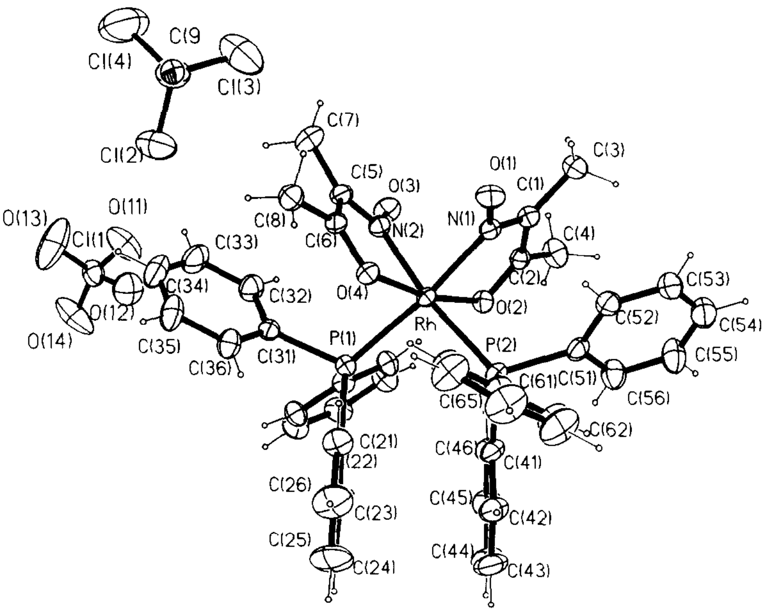

Fig. 2. Molecular structure with labelling scheme for non-hydrogen atoms of [Rh*cis*-(damo)$_2$*cis*-(PPh$_3$)$_2$]ClO$_4$·CHCl$_3$.

Table 2. Selected bond lengths [Å] for [Rh*cis*-(damo)$_2$*cis*-(PPh$_3$)$_2$]ClO$_4$·CHCl$_3$

Rh—N(1)	2.034(3)
Rh—N(2)	2.027(3)
Rh—O(2)	2.028(2)
Rh—O(4)	2.023(2)
Rh—P(1)	2.406(1)
Rh—P(2)	2.401(1)
O(1)—N(1)	1.241(4)
O(2)—C(2)	1.264(4)
N(1)—C(1)	1.337(5)
C(1)—C(2)	1.409(5)
C(1)—C(3)	1.473(5)
C(2)—C(4)	1.488(5)
O(3)—N(2)	1.253(4)
O(4)—C(6)	1.277(4)
N(2)—C(5)	1.337(5)
C(5)—C(6)	1.404(5)
C(5)—C(7)	1.481(5)
C(6)—C(8)	1.490(5)
P(1)—C(21)	1.815(4)
P(1)—C(11)	1.820(4)
P(1)—C(31)	1.841(4)
P(2)—C(61)	1.822(4)
P(2)—C(51)	1.823(4)
P(2)—C(41)	1.823(4)
Cl(1)—O(11)	1.400(4)
Cl(1)—O(12)	1.450(4)
Cl(1)—O(13)	1.355(5)
Cl(1)—O(14)	1.384(5)
Cl(2)—C(9)	1.739(6)
Cl(3)—C(9)	1.744(7)
Cl(4)—C(9)	1.696(7)

in the reaction (**2**), carried out in the presence of the perchloric acid. No IR bands due to the ClO$_4^-$ anion were detected in the isolated complex and its composition has been revealed to be like that of the reaction (**1**), on the basis of elemental analysis and NMR data. The formation of the complex is evidenced by the movement of the 1.87 and 2.31 ppm methyl protons for the Hdamo ligand to higher field upon coordination to the rhodium(III) centre in the compound being discussed. The ^{31}P NMR spectra show one doublet at 18.55 ppm with the ^1J(Rh,P) coupling constant of 92 Hz. Very similar values have been found for the complexes: Rh(dmgH)$_2$(PPh$_3$)$_2$Cl (92 Hz) [2] and [Rh(dmgH)$_2$(PPh$_3$)$_2$]ClO$_4$ (91 Hz) [8] for phosphorus atoms *trans* to each other. This suggests that the substitution reactions of RhCl$_3$·3H$_2$O with the diacetyl monoxime led to the mononuclear complex having one damo$^-$ anion and two Cl$^-$ ions in the equatorial plane and two PPh$_3$ ligands in *trans* axial arrangement, independently of the reaction conditions used, Fig. 1, Ib and/or Ic.

Reaction 3. Compounds of a general formula [Rh(damo)$_2$(PPh$_3$)$_2$]ClO$_4$ have been found to be the products of the reaction between [Rh(H$_2$O)$_6$]$^{3+}$ and Hdamo. The ^{1}H, ^{31}P and ^{13}C NMR spectra showed the formation of two geometrical isomers: **3A** and **3B**. These isomers have always been found to coprecipitate together. In the ^{1}H spectra of the isomer **3A**, the methyl resonances are observed at 0.92 and 1.59 ppm, whereas for **3B** at 0.96 and 1.55 ppm (in CDCl$_3$). The ^{31}P spectra show the doublets at 21.2 ppm (^1JRh,P = 97 Hz) and 20.6 ppm (^1JRh,P = 93 Hz) for the isomers **3A** and **3B**, respectively. We postulate the structures IIa and IIb with two *trans* PPh$_3$ groups

Table 3. Selected angles (°) for [Rh*cis*-(damo)$_2$*cis*-(PPh$_3$)$_2$]ClO$_4$·CHCl$_3$

O(2)—Rh—N(1)	78.67(11)
O(2)—Rh—P(1)	101.61(7)
O(2)—Rh—P(2)	85.22(8)
O(4)—Rh—N(1)	93.12(11)
O(4)—Rh—N(2)	79.11(11)
O(4)—Rh—O(2)	168.80(9)
O(4)—Rh—P(1)	85.57(7)
O(4)—Rh—P(2)	102.37(8)
N(1)—Rh—P(1)	172.77(8)
N(1)—Rh—P(2)	88.80(8)
N(2)—Rh—O(2)	92.24(11)
N(2)—Rh—N(1)	83.21(12)
N(2)—Rh—P(1)	89.56(9)
N(2)—Rh—P(2)	171.96(9)
P(2)—Rh—P(1)	98.42(4)
C(11)—P(1)—Rh	117.16(12)
C(21)—P(1)—Rh	115.40(13)
C(31)—P(1)—Rh	110.31(12)
C(41)—P(2)—Rh	114.21(12)
C(51)—P(2)—Rh	110.00(12)
C(61)—P(2)—Rh	119.28(13)
C(2)—O(2)—Rh	112.4(2)
C(6)—O(4)—Rh	112.3(2)
O(1)—N(1)—Rh	123.3(2)
C(1)—N(1)—Rh	114.3(2)
O(3)—N(2)—Rh	123.4(2)
C(5)—N(2)—Rh	114.3(2)
O(1)—N(1)—C(1)	122.3(3)
O(2)—C(2)—C(4)	117.6(3)
O(2)—C(2)—C(1)	121.1(3)
N(1)—C(1)—C(2)	112.3(3)
N(1)—C(1)—C(3)	120.9(3)
C(1)—C(2)—C(4)	121.3(3)
C(2)—C(1)—C(3)	126.8(3)
O(3)—N(2)—C(5)	122.1(3)
O(4)—C(6)—C(5)	121.0(3)
O(4)—C(6)—C(8)	116.3(3)
N(2)—C(5)—C(6)	112.5(3)
N(2)—C(5)—C(7)	120.1(3)
C(5)—C(6)—C(8)	122.6(3)
C(6)—C(5)—C(7)	127.4(4)
C(11)—P(1)—C(31)	101.4(2)
C(21)—P(1)—C(11)	106.4(2)
C(21)—P(1)—C(31)	104.5(2)
C(61)—P(2)—C(51)	100.3(2)
C(61)—P(2)—C(41)	108.1(2)
C(51)—P(2)—C(41)	102.9(2)
O(13)—Cl(1)—O(14)	111.3(5)
O(13)—Cl(1)—O(11)	111.8(5)
O(14)—Cl(1)—O(11)	109.1(3)
O(13)—Cl(1)—O(12)	107.4(4)
O(14)—Cl(1)—O(12)	110.3(4)
O(11)—Cl(1)—O(12)	106.9(3)
Cl(4)—C(9)—Cl(2)	109.8(4)
Cl(4)—C(9)—Cl(3)	108.3(4)
Cl(2)—C(9)—Cl(3)	110.3(3)

in axial positions (Fig. 1) for the products being described, on the base of the ^1J(Rh,P) coupling constants registered for these species, literature data as well as for a *cis*, *cis* isomer determined both by the X-ray (*vide supra*) and the NMR measurements (*vide infra*). However, X-ray structures of single crystals are needed to distinguish the isomers.

Reaction 4. A condensation product of the diacethyl monoxime and a diaminopropane is 3.9-dimethyl-4,8-diazaundeca-3,8-diene-2,10-dione dioxime H$_2$dopn [11]. Syntheses of many cobalt compounds with this ligand resulted in the description of very interesting Costa-type complexes, models of Vit.B$_{12}$ [14–16]. Attempts to synthesise the rhodium analgoues using RhCl$_3$·3H$_2$O as starting reagent failed to yield the desired species. The reaction between [Rh(H$_2$O$_6$)]$^{3+}$ and H$_2$dopn confirmed the instability of this ligand in the presence of water and acid [11]. The elemental analyses of these reaction products gave excellent agreement with calculated values for the complex of formula [Rh(damo)$_2$(PPh$_3$)$_2$]ClO$_4$ and the species [(H$_2$N)$_2$C$_3$H$_6$]·2HClO$_4$, the second decomposition product of H$_2$dopn. The formation of the latter was also confirmed by the IR and NMR spectra measurements. Fractional crystallisation of the reaction mixture allowed the separation of two different complexes of rhodium(III). The first crystallised product (**4A**) appeared to have identical ^{1}H, ^{31}P and ^{13}C NMR spectra with those of the isomer **3B** described above. The second rhodium(III) species (**4B**), characterised both spectroscopically and crystallographically, has been proved to be the isomer with two Rh—N bonds of the monoxime and two Rh—P bonds of the PPh$_3$ molecules on the rhodium ion *cis* to their own kind, and two Rh—O bonds in the *trans* arrangement (Fig. 2, IId.) In the ^{1}H NMR spectrum the CH$_3$ groups protons are shifted downfield whereas the PPh$_3$ groups in the ^{31}P spectrum are shifted upfield in comparison with the complexes having the triphenylphosphine ligands in the *trans* position to each other. Simultaneously the ^1J(Rh,P) coupling constant has been demonstrated to be *ca.* 10 Hz higher for the former. This suggests the metal to phosphine π-donation to be more effective in the *cis* stereochemistry than in the *trans* arrangement.

These compounds are stable to air as solids when kept in the dark. However, in contrast to the well-known stability of dioximato rhodium(III) complexes, the monoximato derivatives are labile both in solution and when exposed to light.

Results described in this paper raise interesting questions with respect to the factors that determine the isomer distribution for these reaction systems. This is probably related to the reaction conditions, e.g. pH, thermodynamic preference and the mechanism of the exchange process. More detailed kinetics and thermodynamic studies are needed before we can solve these problems. The different substrates used in the syntheses clearly demonstrate the effect of the ligands (Cl$^-$, H$_2$O) coordinated to the rhodium center on the nature of the substitution products. To our knowledge no rhodium(III) complexes with the monoxime ligands have hitherto been reported. Thus the syntheses of rhodium compounds with hetero donor molecules like Hdamo opens new ways for the study of rhodium oximato species.

REFERENCES

1. N. Bresciani Pahor, R. Dreos-Garlatti, S. Geremia and L. Randaccio, *Inorg. Chem.* 1990, **29**, 3437.
2. F. Asaro, R. Dreos-Garlatti, G. Pellizer and G. Tauzher, *Inorg. Chim. Acta* 1993, **211**, 27.
3. B. Giese, J. Hartung, C. Kesselheim, H. J. Lindner and I. Svoboda, *Chem. Ber.* 1993, **126**, 1193.
4. S. Geremia, R. Dreos, L. Randaccio and G. Tauzher, *Inorg. Chim. Acta* 1994, **216**, 125.
5. R. Dreos, G. Tauzher, S. Geremia, L. Randaccio, F. Asaro, G. Pellizer, C. Tavagnacco and G. Costa, *Inorg. Chem.* 1994, **33**, 5404.
6. M. Kubiak, T. Głowiak, M. Moszner, J. J. Ziółkowski, F. Asaro, G. Costa, G. Pellizer and C. Tavagnacco, *Inorg. Chim. Acta*, 1995, **236**, 141.
7. G. Ergun Efe and E. O. Schlemper, *Polyhedron* 1991, **14**, 1611.
8. M. Moszner, F. Asaro, S. Geremia, G. Pellizer and C. Tavagnacco, *Inorg. Chim. Acta*, to be published.
9. A. Nakamura, A. Konishi and S. Otsuka, *J. Chem. Soc., Dalton Trans.* 1979, 488.
10. G. H. Ayres and J. S. Forester, *J. Inorg. Nucl. Chem.* 1957, **3**, 365.
11. E. Uhlig and M. Fridrich, *Z. Anorg. Allg. Chem.* 1966, **343**, 299.
12. G. M. Sheldrick, *Acta Cryst., Sect. A.* 1990, **46**, 467.
13. G. M. Sheldrick, *SHELXL* 93, *program for the refinement of crystal structures*. University of Göttingen, Germany (1994).
14. G. Pellizer, G. R. Tauszik, G. Tauzher and G. Costa, *Inorg. Chim. Acta* 1973, **7**, 60.
15. G. R. Tauszik, G. Pellizer and G. Costa, *J. Inorg. Nucl. Chem.* 1975, **37**, 1532.
16. A. Gerli and L. G. Marzilli, *Inorg. Chem.* 1992, **31**, 1152.
17. M. Dunaj-Jurčo, V. Kettmann, D. Steinborn and M. Ludwig, *Acta Cryst.* 1994, **C50**, 1427.
18. V. Kettmann, M. Dunaj-Jurčo, D. Steinborn and M. Ludwig, *Acta Cryst.* 1994, **C50**, 1239.
19. F. A. Cotton and J. G. Norman, Jr, *J. Am Chem. Soc.* 1971, **93**, 80.