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Synthesis and structure of the mixed bridged diene-rhodium(I) complex [(cod)Rh(μ-Cl)(μ-OAc)Rh(cod)]. Reactions with the modified purine bases N^6,N^6-dimethyladenine and 8-aza-9-methyladenine

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Abstract

The mixed bridged diene-rhodium(I) complex ([cod)Rh(μ-Cl)(μ-OAc)Rh(cod)] (**1**) has been prepared by the reaction of equivalent quantities of $[(cod)RhCl]_2$ and potassium or sodium acetate at reflux in methanol. **1** exhibits an Rh...Rh distance of 3.161(1) Å. Reaction of **1** with N^6,N^6-dimethyladenine (DmadH) yields [(cod)Rh(DmadH)Cl] (**2**), and $[(cod)Rh(\mu\text{-Dmad})]_2$ (**3**), which show N3 and N3,N9 metal binding, respectively. In contrast, reaction of **1** with 8-aza-9-methyladenine (Maad) gives only one product, dimeric $[(cod)Rh(\mu\text{-MaadH}_{-1})Rh(cod)Cl]_2$ (**4**) in which the nucleobase is tridentate with N1, N6 and N7 as rhodium binding sites. The structures of **1**, **2** and **4** have been established by X-ray structural analysis. The rhodium atom in **4** which is bonded to N1 is displaced by 1.08 Å from the plane of the pertinent nucleobase.

Introduction

Chloro-bridged dicarbonyl- and diolefin-rhodium(I) complexes of the type $[L_2RhCl]_2$ (L = CO; L_2 = 1,5-cyclooctadiene (cod), 2,5-norbornadiene (nbd)) [1–3] have frequently been used as starting materials for the synthesis of complexes of the type $[L_2RhCl(B)]$ and $[L_2Rh(B')]_n$ containing donor ligands B and B'H. Examples of bridging nitrogen-donor ligands B' are provided by the pyrazolate anion, Pz^-, in dimeric complexes $[L_2Rh(Pz)]_2$ [4,5] and the imidazolate anion, Im^-, in polymeric complexes $[L_2Rh(Im)]_x$ [6].

The complex $[(cod)Rh(OAc)]_2$ [1] offers an alternative starting material to chloro-bridged diolefin-rhodium(I) dimers. We describe here the synthesis and crystal structure determination of the novel mixed bridged complex [(cod)Rh(μ-

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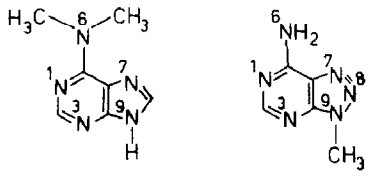
Cl)(μ-OAc)Rh(cod)] (**1**). As part of our continuing studies on the coordination behaviour of modified purine bases we have also investigated the reaction of **1** with N^6,N^6-dimethyladenine (DmadH) and 8-aza-9-methyladenine (Maad). For steric reasons, as a result of the dimethylation of N6 the pyrimidine nitrogen N1 and the



imidazole nitrogen N7 are no longer available as coordination sites in DmadH. Reaction with **1** yields two products.

$$2(\mathbf{1}) + 4\text{DmadH} \rightarrow 2[(\text{cod})\text{Rh}(\text{DmadH})\text{Cl}] + [(\text{cod})\text{Rh}(\mu\text{-Dmad})]_2 + 2\text{HOAc}$$
$$(\mathbf{2}) \qquad (\mathbf{3})$$

In contrast four ring nitrogen atoms, N1,N3,N7 and N8, are potential metal coordination positions in Maad; N6 may be metallated. In this case reaction with **1** leads to the dimeric complex **4** in which MaadH_{-1} is tridentate.

$$2(\mathbf{1}) + 2\text{Maad} \rightarrow [(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})\text{Rh}(\text{cod})\text{Cl}]_2 + 2\text{HOAc}$$
$$(\mathbf{4})$$

We report the crystal structure determination of **2** and **4**.

Results and discussion

The molecular structure of **1** is depicted in Fig. 1. This mixed μ-Cl, μ-OAc-bridged diene-rhodium(I) complex may be prepared by reaction in acetone of either KOAc or $\text{NaOAc} \cdot 10\text{H}_2\text{O}$ with $[(\text{cod})\text{RhCl}]_2$ in equivalent quantities and isolated as orange needle-shaped crystals. Whereas the symmetrically bridged dimer

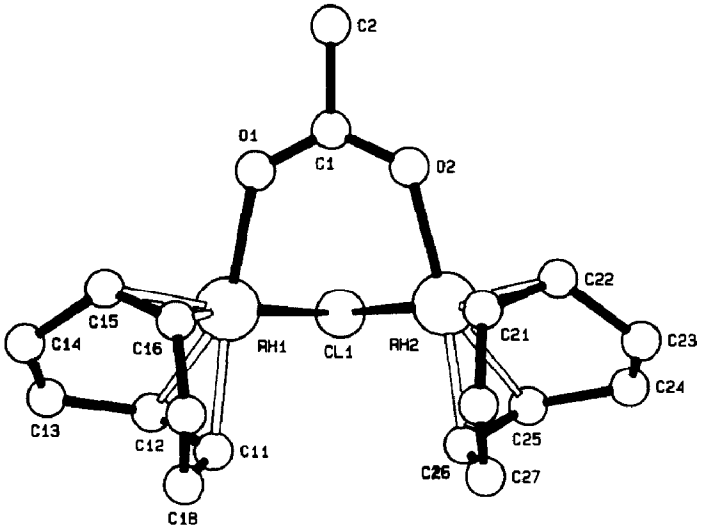


Fig. 1. Molecular structure of [(cod)Rh(μ-Cl)(μ-OAc)Rh(cod)] (**1**).

$[(cod)Rh(OAc)]_2$ may be synthesised by the reaction of **1** with a second equivalent of KOAc in acetone, no further reaction is observed for **1** with $NaOAc \cdot 10H_2O$ under similar conditions even when an excess of sodium acetate is used. Likewise, reaction of $[(cod)RhCl]_2$ with two or more equivalents of sodium acetate only gives the mixed bridged dimer **1**. An explanation for these observations is not immediately apparent. They suggest, however, that the cation may be mechanistically involved in the cleavage of the chlorine bridges and that solvatation effects may be important. An Rh1...Rh2 distance of 3.161(1) Å is observed in **1**. A similar intramolecular Rh...Rh distance of 3.12 Å was observed for the symmetrically bridged dimer $[(CO)_2RhCl]_2$ [7]. Such separations have often been considered as providing evidence for some metal–metal interaction in binuclear rhodium(I) complexes. The two rhodium $(CO)_2RhCl_2$ coordination planes intersect at an angle of 124° in $[(CO)_2RhCl]_2$. In contrast, the deviation from planarity for the central four-membered ring in $[(cod)RhCl]_2$ is much less marked [8], as evidenced by the interplanar angle of 170.5° for the two rhodium coordination planes. As a consequence, $[(cod)RhCl]_2$ exhibits a much larger Rh...Rh separation of 3.50 Å, for which metal–metal interaction can no longer be postulated. The rhodium coordination planes in **1** are inclined at an angle 91.9° to one another, which suggests that a better overlap of the d_{z^2}-orbitals of the individual rhodium atoms should be possible in **1** than in $[(CO)_2RhCl]_2$. These coordination planes exhibit respective dihedral angles of 49.3 and 50.7° with the Rh1, Cl1, Rh2-plane of the central six-membered ring. Symmetrical bridging is exhibited by the OAc-group as evidenced by the Rh–O (2.108(12), 2.093(13) Å) and C–O (1.25(2), 1.25(2) Å) distances and the Rh–O–C angles (129.0(13), 129.5(13)°). The OAc-group is inclined at 7.6° to the least-squares plane through the atoms Rh1,Rh2,O1 and O2; distances from the latter plane are Rh1 −0.017, Rh2 0.018, O1 0.025, O2 −0.025 Å.

The close structural similarity of square-planar d^8 *cis*-rhodium(I) complexes such as $[(cod)Rh(NH_3)Cl]$ or [(cod)Rh(acac)] to *cis*-platinum(II) complexes with documented antitumour activity has led to the screening of a number of these derivatives [9]. For instance, [(cod)Rh(acac)] displays activity against the Ehrlich ascites test system superior to that of *cis*-$[PtCl_2(NH_3)_2]$. Platinum binding of DNA guanine nitrogens N7 has often been postulated to explain the antitumor properties of the latter complex [10]. We are thus interested in studying the coordination behaviour of purine and pyrimidine bases in square-planar rhodium(I) complexes. Carbonylrhodium(I) complexes of the type $[RhCl(CO)_2B]$ (B = nucleobase or nucleoside) [11–14] and $[(CO)Rh(PPh_3)_2B]PF_6$ [15] have been reported. However, reaction of [(cod)Rh(acac)] with nucleobases must lead to metallation and the formation of species such as $[(cod)Rh(BH_{-1})(B)]$ or $[(cod)Rh(BH_{-1})]_n$ in which the deprotonated ligand BH_{-1} will be respectively mono- or bi-dentate. Such complexes of nucleobases have, to our knowledge, not previously been characterized. As intramolecular chelate formation (e.g. N6,N7 for adenine O6, N1 for guanine) is sterically unfavourable for deprotonated purine nucleosides BH_{-1}, these must adopt a bridging function in their complexes $[(cod)Rh(BH_{-1})]_n$, which will be oligomeric or polymeric. For DNAs the formation of species $[(cod)Rh(BH_{-1})\ (B')]$ in which one or both of the ligands B and B′ are nucleobases may be postulated.

Reaction of **1** with N^6,N^6-dimethyladenine (DmadH) leads, as expected, to the formation of two complexes [(cod)Rh(DmadH)Cl] (**2**) and $[(cod)Rh(\mu\text{-Dmad})]_n$ (**3**), which can be separated because of the insolubility of the oligomeric species **3** in the

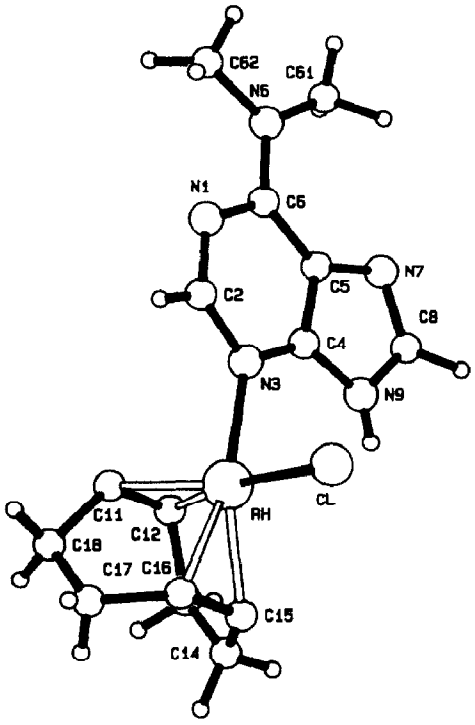


Fig. 2. Molecular structure of [(cod)Rh(DmadH)Cl)] (**2**).

reaction medium methanol. As N1 and N7 are not available as coordination sites for steric reasons in DmadH, N3 must be coordinated and N9 metallated in **3**. Suitable crystals for an X-ray structural analysis could not be grown. However, reaction of **3** with carbon monoxide gave $[(CO)_2Rh(\mu\text{-Dmad})]_n$ and subsequent replacement of one CO ligand by Ph_3P yielded $[(CO)Rh(PPh_3)(\mu\text{-Dmad})]_2$, for which a dimeric structure was established by X-ray structural analysis [16]. These findings will be reported in a subsequent paper. It seems reasonable to assume that $[(cod)Rh(\mu\text{-Dmad})]_n$ (**3**) is also dimeric.

Figrue 2 depicts the molecular structure of **2** in which N3 of the pyrimidine ring is coordinated. The heterocycle is twisted to a dihedral angle of 85.6° relative to the rhodium coordination plane. A *trans* influence is apparent for the Rh–C(cod) distances. Those *trans* to Cl are significantly shorter (2.084(7), 2.087(7) Å) than those *trans* to N3 (2.120(7), 2.126(7) Å). The greater degree of π-back-bonding in the rhodium interaction with the former olefinic C–C bond is underlined by the (albeit not significantly) longer C11–C12 distance of 1.379(12) Å in comparison to C15–C16 (1.365(11) Å).

8-Aza-9-methyladenine (Maad) offers N6 as a potential metallation site and N1, N3, N7 and N8 as potential coordination sites for metal atoms. However, replacement of the 8-CH function in purines by an aza-nitrogen leads to profound alterations in the chemical and biological properties of the resultant bases. For instance, the effective antineoplastic properties of various 8-azapurine nucleosides have been intensively studied [17]. Molecular orbital calculations have demonstrated that N7 and N8 in H9-tautomers of 8-azapurines carry virtually no residual charge [18,19]. Systematic studies of the interaction of the methylmercury(II) cation with

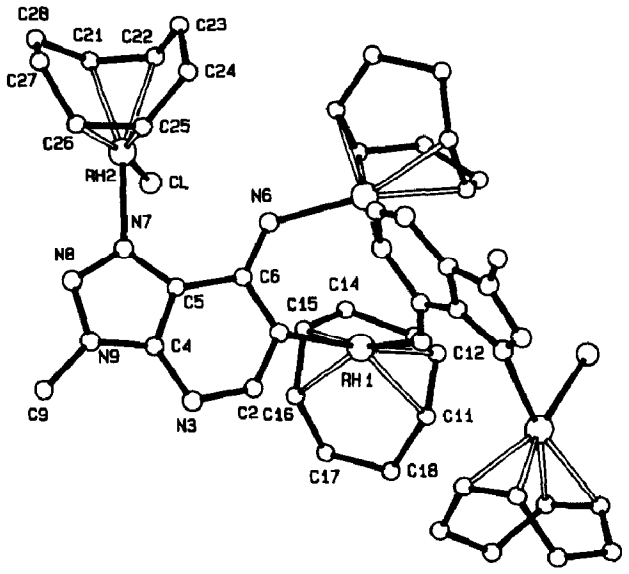


Fig. 3. Molecular structure of $[(cod)Rh(\mu\text{-}MaadH_{-1})Rh(cod)Cl]_2$ (**4**).

8-azaadenine and its 9-methyl derivative provided no evidence for N7 or N8 metal binding [20,21]. These investigations indicated that if N9 is bonded to either an alkyl group, a proton or a metal atom, then either N1 or N3 of the pyrimidine ring will be the chosen binding site. We have, indeed, identified N1 and N3, respectively, as binding sites in complexes [RhCl(cod)B] (B = Maad and 8-aza-9-benzyladenine) [14]. Metallation of N6 by CH_3Hg^+ was found to lead to an enhancement of the basicity of N1 relative to N3 [21]. The above findings and a consideration of the relative bulkiness of cod led us to believe that reaction of **1** with Maad would yield two products as for DmadH, namely a monomeric species analogous to **2** with N1 as metal coordination site and an oligomeric species analogous to **3** with N1,N6-binding. To our surprise the reaction between **1** and Maad in 1/1 ratio yielded only one product, namely the dimeric species $[(cod)Rh(\mu\text{-}MaadH_{-1})Rh(cod)Cl]_2$ (**4**), which exhibits N1,N6,N7-binding. **4** is also obtained as the sole product when a 1/2 ratio of **1** and Maad is used.

The structure of **4** is depicted in Fig. 3. **4** exhibits crystallographic C_2 symmetry leading to the formation of a central eight-membered ring. The coordination of N1 by Rh1 is most remarkable, as the rhodium atom is displaced by 1.08 Å from the plane of heterocycle. As a result the Rh1–N1 bond makes an angle of 28.9° with this base plane and Rh–N distances indicate that this bond is weaker than Rh2–N7 (2.13(1) vs. 2.09(1) Å). It must be assumed that this unusual coordination geometry is necessary in order to reduce steric contacts in the central ring. The bond angle C2–N1–Rh1 with a value of 113.0(8) is markedly smaller than the neighbouring angle C6–N1–Rh1 (121.2(9)°). A *trans* influence is apparent for the Rh2 coordination sphere. Those Rh2–C(cod) distances *trans* to Cl are markedly shorter (2.08(2), 2.09(2) Å) than those *trans* to N7 (2.14(1), 2.16(2) Å).

Metal binding to N7 (or N8) has not previously been observed for 8-azaadenine derivatives in which N9 is bonded to either an alkyl group, a proton or a metal atom [20,21]. Our results indicate that dimeric complexes such as **1**, $[(cod)Rh(OAc)]_2$ or

$[(cod)RhCl]_2$ should be capable of metallating N6 of adenine bases. The same should also be the case for monomeric [(cod)Rh(acac)], which displays antitumour properties. Whereas N1 will be the preferred ring binding site for 8-aza-9-methyladenine, N7 of the imidazole ring should compete with this pyrimidine nitrogen for adenosine (ado) derivatives. Oligomeric species $[(cod)Rh(adoH_{-1})]_n$ with either N1,N6-binding as in **4** or N7,N6-binding as in tetrameric $[(CO)_2Rh(3mad)]_4$ (3madH = 3-methyladenine) [16] should be feasible. Interestingly, the latter binding mode should not prevent the participation of adenine in Watson–Crick base pairing.

Experimental

IR spectra were recorded as 1% KBr discs on a Perkin–Elmer 297 spectrometer. ^1H NMR spectra were recorded on a Bruker WP 200 spectrometer at 20 °C. Elemental analyses were performed with a Perkin–Elmer 240 apparatus. $[(cod)RhCl]_2$ [1] and 8-aza-9-methyladenine [22] were prepared as described previously; $RhCl_3 \cdot 3H_2O$ was a gift from Degussa AG. N^6,N^6-Dimethyladenine was purchased from Sigma Chemie GmbH and used as received.

*Synthesis of [(cod)Rh(μ-Cl)(μ-OAc)Rh(cod)] (**1**)*

A solution of 200 mg (0.4 mmol) of $[(cod)RhCl]_2$ and 40 mg (0.4 mmol) of KOAc in 20 ml of acetone was refluxed for 3 h. The solvent was removed and the orange solid recrystallised from ethyl acetate to yield orange needle shaped crystals of **1** (yield 86%). **1** can also be obtained in similar yields by use of 110 mg (0.4 mmol) $NaOAc \cdot 10H_2O$ instead of KOAc. Anal. found: C, 41.8; H, 5.24. $C_{18}H_{27}O_2ClRh_2$ (M, 516.7) calcd.: C, 41.84; H, 5.27%. IR: 2990 m, 2920 m, 2860 m, 2810 m, ν(cod CH), 1550 s, ν(CO), 1410 s, ν(C=C) cm^{-1}. ^1H NMR (TMS, CD_2Cl_2): 1.72 (s, 3H, CH_3), 1.82 (s, 4H, cod CH_2), 1.87 (s, 4H cod CH_2), 2.45–2.78 (8H, cod CH_2), 4.06 broad (s, 4H, cod CH), 4.24 broad (s, 4H, cod CH).

*Reaction of **1** with KOAc*

A solution of 50 mg (0.095 mmol) of **1** and 19 mg (0.19 mmol) of KOAc in 15 ml of acetone was refluxed for 2 h. The solvent was removed and the solid recrystallised from ethyl acetate to yield prismatic cyrstals of $[(cod)Rh(OAc)]_2$ (yield 93%) (Lit. [1]).

*Reaction of **1** with $NaOAc \cdot 10H_2O$*

A solution of 50 mg (0.095 mmol) of **1** and 51 mg (0.19 mmol) of $NaOAc \cdot 10H_2O$ in 15 ml acetone was refluxed for 2 h. The solvent was removed and the solid recrystallised from ethyl acetate to give quantitative recovery of orange needles of the starting material **1**.

*Reaction of **1** with N^6,N^6-dimethyladenine*

A mixture of 197 mg (0.38 mmol) of **1** and 124 mg (0.76 mmol) of N^6,N^6-dimethyladenine (DmadH) in 10 ml of methanol was stirred for 15 h. The orange solid was filtered off, washed with methanol and dried. It was characterised as $[(cod)Rh(\mu\text{-}Dmad)]_2$ (**3**) (yield 42% with respect to **1**). The yellow solution was

reduced in volume and cooled to 6 °C to yield yellow crystals of [(cod)Rh(DmadH)Cl] (**2**) (yield 38% with respect to **1**).

2, Anal. found.: C, 44.0; H, 5.14; N, 16.9. $C_{15}H_{21}N_5ClRh$ (M, 409.7) calcd.: C, 43.97; H, 5.17; N, 17.9%. ^1H NMR (TMS,CD_2Cl_2): 1.80 (s, 2H, cod CH_2), 1.85 (s, 2H, cod CH_2), 2.49 (4H, cod CH_2), 3.29 broad (s, 3H, Dmad CH_3), 3.74 broad (s, 3H, Dmad CH_3), 4.19 (s, 4H, cod CH), 7.82 broad (s, Dmad H2), 8.15 (s, Dmad H8), 11.75 broad (s, Dmad H9).

3, Anal. found.: C, 48.4; H, 5.53; N, 18.4. $C_{30}H_{40}N_{10}Rh_2$ (M, 746.5) calcd.: C, 48.27; H, 5.40; N, 18.7%. ^1H NMR, (TMS, $CDCl_3$): 1.84–2.29 (several m, 4H cod CH_2), 2.48–3.04 (several m, 4H cod CH_2), 3.37 (s, 6H, Dmad CH_3), 4.06–4.74 (4H, cod CH), 7.82, 7.90 (s, 1H, Dmad H2), 8.33, 8.45 (s, 1H, Dmad H8).

*Reaction of **1** with 8-aza-9-methyladenine*

A mixture of 196 mg (0.38 mmol) of **1** and 57 mg (0.38 mmol) of 8-aza-9-methyladenine (Maad) in 10 ml of methanol was stirred for 15 h. The orange solid was filtered off, washed with methanol and dried (yield 81%). Crystals of **4** suitable for X-ray structural analysis were obtained by recrystallisation from a chloroform/acetonitrile mixture. **4** was characterised as $[(cod)Rh(\mu\text{-}MaadH_{-1})Rh(cod)Cl]_2 \cdot 2CHCl_3$. Anal. found.: C,37.2; H, 4.36; N, 12.0. $C_{44}H_{60}N_{12}Cl_8Rh_4$ (M, 1452.3) calcd.: C, 36.39; H, 4.16; N, 11.57%. ^1H NMR (TMS, $CDCl_3$): 1.6–2.7 (8H, cod CH_2), 3.95, 4.0 (s, 3H, Maad CH_3), 4.1–4.9 (4H, cod CH), 8.21 (s, 1H, Maad H2), 8.81 (s, 1H, Maad H6).

X-Ray structural analyses

Crystal and refinement data for **1**, **2** and **4** are summarized in Table 1. Unit cell constants were obtained from a least-squares fit to the settings of 25 reflections recorded on an Enraf–Nonius CAD4 diffractometer. Intensity data were collected

Table 1

Crystal and refinement data

Compound	**1**	**2**	**4**
Space group	$P2_1/n$	$P2_1/n$	$Pccn$
a (Å)	12.956(4)	11.364(2)	14.296(2)
b (Å)	18.712(3)	7.474(1)	22.044(2)
c (Å)	7.555(1)	19.496(3)	16.991(3)
β (°)	90.18(2)	94.29(4)	90
V (Å^3)	1831.6(11)	1651.4(8)	5354(2)
Z	4	4	4
D_c(g.cm^{-3})	1.87	1.65	1.80
Radiation	Mo-K_α	Mo-K_α	Cu-K_α
μ (cm^{-1})	19.3	11.8	141.8
Scan method	θ-2θ	θ-2θ	ω
$2\theta_{max.}$(°)	50	50	130
Reflections measured	3202	2876	4541
Reflections observed	2151	2308	3496
Rejection criterion	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 3\sigma(F_o^2)$	$F_o^2 < 3\sigma(F_o^2)$
R	0.058	0.035	0.057
R_w	0.058	0.036	0.058
p	0.017	0.010	0.012

Table 2

Atom coordinates with equivalent isotropic temperature factors ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}
1				
Rh1	0.0615(1)	0.3149(1)	0.0887(1)	30(1)
Rh2	−0.1825(1)	0.3111(1)	0.0872(1)	38(1)
Cl1	−0.0606(2)	0.3250(2)	−0.1515(4)	43(2)
O2	−0.1436(6)	0.2030(4)	0.1117(12)	47(5)
O1	0.0285(7)	0.2055(4)	0.1227(13)	51(6)
C1	−0.0565(11)	0.1739(6)	0.1123(19)	48(8)
C2	−0.0566(12)	0.0925(6)	0.1103(2)	60(9)
C11	0.0774(11)	0.4266(6)	0.1136(19)	48(8)
C12	0.1494(11)	0.3993(7)	−0.0129(20)	51(9)
C13	0.2657(11)	0.3864(8)	0.0280(22)	64(10)
C14	0.2861(10)	0.3392(10)	0.1794(30)	104(14)
C15	0.1951(11)	0.2943(7)	0.2482(17)	44(8)
C16	0.1138(11)	0.3169(8)	0.3510(17)	53(9)
C17	0.1021(13)	0.3982(8)	0.4331(19)	64(10)
C18	0.1071(13)	0.4479(8)	0.3009(20)	71(11)
C21	−0.2300(11)	0.3088(7)	0.3508(18)	51(8)
C22	−0.3124(10)	0.2878(7)	0.2378(16)	40(7)
C23	−0.4050(11)	0.3381(8)	0.1998(21)	59(10)
C24	−0.3878(11)	0.3791(8)	0.0296(20)	62(10)
C25	−0.2737(11)	0.3945(7)	−0.0077(18)	49(8)
C26	−0.2030(11)	0.4219(6)	0.1128(18)	49(8)
C27	−0.2311(12)	0.4419(8)	0.3012(20)	65(10)
C28	−0.2262(12)	0.3821(9)	0.4356(19)	65(10)
2				
Rh	0.1317(1)	0.2105(1)	0.6460(1)	34(1)
Cl	0.3070(1)	0.2694(2)	0.7168(1)	39(1)
N1	0.3292(4)	0.1100(6)	0.4669(2)	40(3)
N3	0.2358(4)	0.1001(6)	0.5721(2)	37(2)
N6	0.4117(4)	−0.1326(7)	0.4158(2)	47(3)
N7	0.3352(4)	−0.3434(6)	0.5445(2)	47(3)
N9	0.2437(4)	−0.1931(7)	0.6234(2)	43(3)
C2	0.2736(5)	0.1806(8)	0.5166(3)	44(3)
C4	0.2643(4)	−0.0734(7)	0.5742(2)	33(3)
C5	0.3224(4)	−0.1659(7)	0.5250(3)	35(3)
C6	0.3551(4)	−0.0656(8)	0.4686(3)	37(3)
C8	0.2883(6)	−0.3514(8)	0.0630(3)	51(4)
C11	−0.0064(6)	0.2471(10)	0.5708(3)	63(4)
C12	−0.0154(5)	0.0793(10)	0.5994(3)	60(4)
C13	−0.1005(8)	0.0327(15)	0.6528(5)	102(7)
C14	−0.0772(8)	0.0976(18)	0.7205(4)	98(7)
C15	0.0258(5)	0.2216(10)	0.7309(3)	54(4)
C16	0.0317(5)	0.3892(10)	0.7035(3)	56(4)
C17	−0.0623(10)	0.4740(14)	0.6575(6)	108(8)
C18	−0.0813(10)	0.4083(16)	0.5886(5)	108(7)
C61	0.4426(7)	−0.3192(11)	0.4114(4)	62(5)
C62	0.4385(7)	−0.0169(14)	0.3592(4)	63(5)
4·2$CHCl_3$				
Rh1	0.2263(1)	0.6778(1)	0.5625(1)	31(1)
Rh2	−0.0416(1)	0.9007(1)	0.6632(1)	35(1)
Cl	−0.0723(2)	0.8516(2)	0.5424(2)	74(2)
Cl31	0.3601(5)	0.2849(3)	−0.0691(5)	193(7)

Table 2 (continued)

Atom	x	y	z	U_{eq}
4·2$CHCl_3$				
Cl32	0.3440(4)	0.3787(3)	0.0337(4)	155(5)
Cl33	0.3547(5)	0.3957(3)	−0.1311(4)	190(6)
N1	0.1576(5)	0.7139(3)	0.6635(5)	29(4)
N3	0.0576(6)	0.6720(3)	0.7641(5)	39(5)
N6	0.1453(5)	0.8139(3)	0.6180(5)	30(4)
N7	−0.0355(5)	0.8158(3)	0.7177(5)	40(5)
N8	−0.0974(6)	0.7974(4)	0.7705(6)	52(6)
N9	−0.0715(6)	0.7407(4)	0.7933(5)	45(5)
C2	0.1298(7)	0.6712(4)	0.7138(6)	34(5)
C4	0.0076(7)	0.7247(4)	0.7559(6)	35(5)
C5	0.0309(6)	0.7729(4)	0.7076(6)	29(5)
C6	0.1128(6)	0.7702(4)	0.6611(6)	32(5)
C9	−0.1254(10)	0.7077(6)	0.8513(8)	74(9)
C11	0.2800(6)	0.5996(4)	0.5045(7)	45(6)
C12	0.2847(7)	0.6500(5)	0.4525(7)	49(7)
C13	0.2163(8)	0.6590(6)	0.3829(8)	60(8)
C14	0.1271(9)	0.6941(5)	0.4064(7)	57(8)
C15	0.1027(7)	0.6904(5)	0.491397)	47(7)
C16	0.0941(6)	0.6348(5)	0.5328(7)	46(6)
C17	0.1065(7)	0.5730(5)	0.4967(8)	52(7)
C18	0.2081(7)	0.5508(5)	0.5031(9)	61(8)
C21	−0.0930(9)	0.9852(5)	0.6182(8)	60(8)
C22	0.0021(9)	0.9814(5)	0.6016(8)	61(8)
C23	0.0741(10)	1.0157(6)	0.6480(11)	89(11)
C24	0.1127(11)	0.9804(7)	0.7160(10)	94(12)
C25	0.0450(10)	0.9355(6)	0.7506(8)	68(9)
C26	−0.0481(10)	0.9466(5)	0.7708(7)	61(8)
C27	−0.0922(12)	1.0100(6)	0.7648(9)	80(10)
C28	−0.1364(9)	1.0204(5)	0.6856(7)	66(8)
C30	0.3132(13)	0.3532(9)	−0.0553(14)	127(17)

on the diffractometer at varied scan rates using Mo-K_α radiation for **1** and **2** and Cu-K_α radiation for **4**. Three selected reflections were monitored at regular intervals during data collection; no significant decreases in intensity were observed. Empirical absorption corrections were performed for all data sets. The structures were solved by direct methods and difference syntheses and refined by full-matrix least-squares. The asymmetric unit of **4** contains one chloroform molecule of crystallization. Anisotropic temperature factors were introduced for all non-hydrogen atoms in **1**, **2** and **4**. Hydrogen atom positions were refined freely for **2**; for **1** and **4** they were included, where possible, at calculated positions with d(C–H) 1.08 Å. Terminal reliability indices are listed in Table 1 where $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2}$ with weights given by $w = [\sigma^2(F_o) + p^2 F_o^2]^{-1}$. Final difference syntheses were effectively contourless. Analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion were taken from ref. [23]. Calculations were performed with SHELX-76 [24] and with local programs. Relevant atomic coordinates are listed in Table 2 and bond lengths to the rhodium atoms in Table 3. Full details of the X-ray analyses are available from Fachinfor-

Table 3

Bond lengths (Å) to the rhodium atoms

1			
Rh1–Cl1	2.411(5)	Rh2–Cl1	2.415(5)
Rh1–O1	2.108(12)	Rh2–O2	2.093(13)
Rh1–C11	2.11(2)	Rh2–C21	2.09(2)
Rh1–C12	2.10(2)	Rh2–C22	2.08(2)
Rh1–C15	2.14(2)	Rh2–C25	2.08(2)
Rh1–C16	2.09(2)	Rh2–C26	2.10(2)
2			
Rh–Cl	2.378(2)	Rh–N3	2.100(5)
Rh–C11	2.084(7)	Rh–C15	2.120(7)
Rh–C12	2.087(7)	Rh–C16	2.126(7)
4			
Rh1–N1	2.13(1)	Rh1–N6	2.07(1)
Rh1–C11	2.13(1)	Rh1–C15	2.16(1)
Rh1–C12	2.14(10	Rh1–C16	2.17(1)
Rh2–Cl	2.360(5)	Rh2–N7	2.09(1)
Rh2–C21	2.14(1)	Rh2–C22	2.16(2)
Rh2–C25	2.08(2)	Rh2–C26	2.09(2)

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