

Synthesis and structural characterization of diene- and carbonyl-rhodium(I) complexes containing bridging adeninate ligands

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Abstract

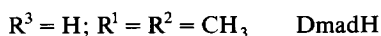
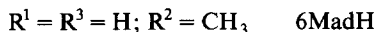
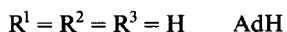
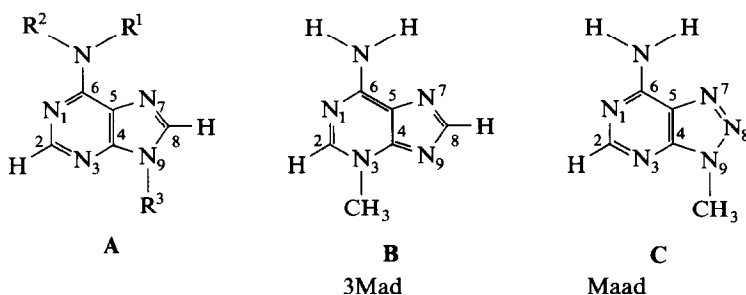
Diene- and dicarbonyl-rhodium(I) complexes $[(\text{diene})\text{Rh}(\mu\text{-BH}_{-1})]_2$ (diene = cod, nbd) and $[(\text{CO})_2\text{Rh}(\mu\text{-BH}_{-1})]_2$ have been prepared by the reaction of $[(\text{diene})\text{Rh}(\text{acac})]$ or $[(\text{CO})_2\text{Rh}(\text{acac})]$ with the adenine derivatives: adenine (AdH), N^6 -methyladenine (6MadH) and N^6, N^6 -dimethyladenine (DmadH). These dimeric complexes exhibit N3, N9 coordination of the bridging adeninate ligands as demonstrated by an X-ray structural study of $[(\text{CO})\text{Rh}(\mu\text{-Dmad})(\text{PPh}_3)]_2$ **3c**, prepared by substitution of a carbonyl ligand in $[(\text{CO})_2\text{Rh}(\mu\text{-Dmad})]_2$ **3b** by PPh_3 . In contrast, a tetrameric structure was observed for $[(\text{CO})_2\text{Rh}(\mu\text{-3madH}_{-1})]_4$ **4** (3mad = 3-methyladenine), in which the 3madH $_{-1}$ anions are coordinated at N6 and N7. When N7 coordination is unfavourable and N9 unavailable, which is the case for 8-aza-9-methyladenine (Maad), N1, N6 binding may be observed, as established by an X-ray structural study of $[(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})]_2$ **5**. However, in order to achieve this coordination mode it is necessary for the substituted exocyclic amino groups (N6) to twist by an average angle of 31.2° out of the base plane.

Introduction

The close electronic and structural similarity of square-planar d^8 *cis*-rhodium(I) complexes such as $[(\text{cod})\text{RhCl}(\text{NH}_3)]$ (cod = 1,5-cyclooctadiene) or $[(\text{cod})\text{Rh}(\text{acac})]$ to *cis*-platinum(II) complexes showing antitumour activity has led to the screening of a number of these derivatives [1]. For instance, $[(\text{cod})\text{Rh}(\text{acac})]$ displays activity against the Ehrlich ascites test system superior to that of *cis*- $[\text{PtCl}_2(\text{NH}_3)_2]$. Platinum binding of DNA guanine nitrogen atoms N7 has frequently been postulated in order to explain the cancerostatic properties of the latter complex [2]. We are interested in the coordination behaviour of purine and pyrimidine bases in square-planar rhodium(I) complexes. Dicarbonylrhodium(I) complexes of the type $[(\text{CO})_2\text{RhCl}(\text{B})]$ (B = nucleobase) have been synthesised and structurally characterised [3–6]. For B = guanine, a complex $[(\text{CO})_2\text{RhCl}]_2\text{B}$ with a bridging nucleobase ligand was prepared, for which bonding to the metal of one pyrimidine

and one imidazole nitrogen was indicated by the ^1H NMR and IR spectra [4]. Complexes of the type $[(\text{CO})\text{Rh}(\text{PPh}_3)_2\text{B}]\text{PF}_6$ have been reported by Abbott and Woods [7], who interpreted ^{13}C NMR data for B = guanosine, inosine, or 1-methyl-inosine in terms of O6-binding.

Reaction of $[(\text{cod})\text{Rh}(\text{acac})]$ with nucleobases must lead to metallation and the formation of species such as $[(\text{cod})\text{Rh}(\text{BH}_{-1})(\text{B})]$ or $[(\text{cod})\text{Rh}(\text{BH}_{-1})]_n$, in which the deprotonated ligand BH_{-1} will be respectively mono- or bi-dentate. 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 mode in their complexes $[(\text{cod})\text{Rh}(\text{BH}_{-1})]_n$, which will be oligomeric or polymeric. For DNAs the formation of species $[(\text{cod})\text{Rh}(\text{BH}_{-1})(\text{B}')]_n$, in which one or both of the ligands B and B' are nucleobases, may be postulated. We have recently demonstrated that reaction of the novel mixed bridged diene-rhodium(I) complex $[(\text{cod})\text{Rh}(\mu\text{-Cl})(\mu\text{-OAc})\text{Rh}(\text{cod})]$ [8] with N^6, N^6 -dimethyladenine (DmadH) yields $[(\text{cod})\text{RhCl}(\text{DmadH})]$ with N3 coordination (X-ray structural determination) and $[(\text{cod})\text{Rh}(\mu\text{-Dmad})]_2$ for which N3, N9 metal binding was proposed [8]. In contrast, reaction of $[(\text{cod})\text{Rh}(\mu\text{-Cl})(\mu\text{-OAc})\text{Rh}(\text{cod})]$ with 8-aza-9-methyladenine (Maad) leads to only one product, dimeric $[(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})\text{Rh}(\text{cod})\text{Cl}]_2$, in which the nucleobase is tridentate with N1, N6, and N7 as rhodium-binding sites [8].



Our results indicate that dimeric complexes such as $[(\text{diene})\text{Rh}(\text{OAc})]_2$ (diene = cod, norbornadiene nbd) or $[(\text{CO})_2\text{Rh}(\text{OAc})]_2$ should be capable of metallating either the amino nitrogen N6 or the imidazole nitrogen N9 of adenine bases. The pyrimidine nitrogens N1 and N3 and the imidazole nitrogen N7 are available as potential further metal coordination sites. We have now prepared a series of oligomeric species $[\text{L}_2\text{Rh}(\text{BH}_{-1})]_n$ ($n = 2, 4$; $\text{L}_2 = \text{cod}, \text{nbd}, (\text{CO})_2$) for the adenine derivatives AdH (adenine), 6MadH (N^6 -methyladenine), DmadH (N^6, N^6 -dimethyladenine), 3Mad (3-methyladenine) and Maad (8-aza-9-methyladenine). X-ray structural determinations were performed on the complexes $[(\text{CO})_2\text{Rh}(\mu\text{-3MadH}_{-1})]_4$ **4**, $[(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})]_2$ **5** and on the PPh_3 derivative $[(\text{CO})\text{Rh}(\mu\text{-Dmad})(\text{PPh}_3)]_2$ **3c**. These compounds display respectively N6, N7, N6, N1 and N9, N3 pairs of metal-binding sites.

Experimental

IR spectra were recorded with 1% KBr discs on a Perkin–Elmer 881 spectrometer. ^1H NMR spectra were recorded on a Bruker AM 400 spectrometer at 20°C ; δ values are in ppm. Elemental analyses were performed with a Perkin–Elmer 240 instrument and the results are listed in Table 1. $[(\text{cod})\text{RhCl}]_2$ [9], $[(\text{cod})\text{Rh}(\text{acac})]$ [10], $[(\text{nbd})\text{Rh}(\text{acac})]$ [10], $[(\text{CO})_2\text{Rh}(\text{acac})]$ [11], $[(\text{CO})\text{Rh}(\text{acac})(\text{PPh}_3)]$ [10], $[(\text{cod})\text{Rh}(\mu\text{-Dmad})]_2$ [8] and Maad [12] were prepared as described previously. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was a gift from Degussa AG. AdH, 6MadH, DmadH and 3Mad were purchased from Sigma Chemie GmbH and used as received.

Preparation of complexes $[(\text{diene})\text{Rh}(\mu\text{-BH}_{-1})]_2$; diene = cod, nbd; B = AdH, 6MadH, DmadH

In a typical preparation 56 mg (0.19 mmol) of $p(\text{nbd})\text{Rh}(\text{acac})$ were added to 26 mg (0.19 mmol) of adenine in 5 ml of methanol. A red precipitate was immediately formed. After 15 h stirring at room temperature, the solid **1** was isolated by centrifugation, washed with methanol, and dried (yield 84%).

1 $[(\text{nbd})\text{Rh}(\mu\text{-Ad})]_2$, $\text{C}_{24}\text{H}_{24}\text{N}_{10}\text{Rh}_2$ (*M*, 658.3), ^1H NMR ($\text{DMSO}-d_6$, TMS), 1.41 (s, 4H, nbd CH_2), 4.25–4.50 (12H, nbd CH), 6.85 (s, 4H, Ad H6), 7.75 (s, 2H, Ad H8) 8.17, 8.21 ppm (2s, 2H, Ad H2).

2a $[(\text{cod})\text{Rh}(\mu\text{-6Mad})]_2$, $\text{C}_{28}\text{H}_{36}\text{N}_{10}\text{Rh}_2$ (*M*, 718.5), yield 82%, ^1H NMR (CDCl_3 , TMS), 1.98 (br, 8H, cod CH_2), 2.55 (br, 8H, cod CH_2), 3.18, 3.19 (2d, 6H, 6Mad CH_3), 3.49–5.14 (8H, cod, CH) 7.43, 7.59 (2s, 2H, 6Mad H8), 8.06, 8.20 (2s, 2H, 6Mad H2), 8.23, 8.80 ppm (2q, 2H, 6Mad H6, $^2J(\text{HH}) = 4.9$ Hz).

2b $[(\text{nbd})\text{Rh}(\mu\text{-6Mad})]_2$, $\text{C}_{26}\text{H}_{28}\text{N}_{10}\text{Rh}_2$ (*M*, 686.4), yield 85%, ^1H NMR (CDCl_3 , TMS), 1.51 (s, 4H, nbd CH_2), 3.04, 3.06 (2s, 6H, 6Mad CH_3), 4.28–4.53 (12H, nbd, CH) 7.71, 7.75 (2s, 2H, 6Mad H8), 8.26, 8.30 ppm (2s, 2H, 6Mad H2).

3a $[(\text{nbd})\text{Rh}(\mu\text{-Dmad})]_2$, $\text{C}_{28}\text{H}_{32}\text{N}_{10}\text{Rh}_2$ (*M*, 714.4), yield 81%, ^1H NMR (CD_2Cl_2 , TMS), 1.48 (s, 4H, nbd CH_2), 3.34 (s, 12H, Dmad CH_3) 4.28–4.52 (12H, nbd CH), 7.67, 7.68 (2s, 2H, Dmad H8), 8.17, 8.20 ppm (2s, 2H, Dmad H2).

Preparation of $[(\text{CO})_2\text{Rh}(\mu\text{-Dmad})]_2$ **3b** and $[(\text{CO})\text{Rh}(\mu\text{-Dmad})(\text{PPh}_3)]$ **3c**

3b. 50 mg (0.19 mmol) of $[(\text{CO})_2\text{Rh}(\text{acac})]$ were added to 31 mg (0.19 mmol) of N^6, N^6 -dimethyladenine in 5 ml of methanol to give an orange solution, which was

Table 1

Analytical data for rhodium(I) complexes

Compound		(Anal. found (calc.)(%)		
		C	H	N
$[(\text{nbd})\text{Rh}(\mu\text{-Ad})]_2$	1	43.8(43.78)	3.78(3.68)	20.5(21.28)
$[(\text{cod})\text{Rh}(\mu\text{-6Mad})]_2$	2a	46.0(46.81)	5.00(5.05)	18.8(19.50)
$[(\text{nbd})\text{Rh}(\mu\text{-6Mad})]_2$	2b	45.1(45.49)	4.33(4.11)	19.5(20.41)
$[(\text{nbd})\text{Rh}(\mu\text{-Dmad})]_2$	3a	47.2(47.07)	4.48(4.51)	19.6(19.61)
$[(\text{CO})_2\text{Rh}(\mu\text{-Dmad})]_2$	3b	33.6(33.66)	2.62(2.51)	21.6(21.81)
$[(\text{CO})\text{Rh}(\mu\text{-Dmad})(\text{PPh}_3)]_2$	3c	55.4(56.23)	4.32(4.17)	12.2(12.61)
$[(\text{CO})_2\text{Rh}(\mu\text{-3MadH}_{-1})]_4$	4	30.5(30.83)	2.69(2.44)	20.7(21.15)
$[(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})]_2$	5	42.4(43.34)	4.70(4.76)	23.0(23.33)

Microanalyses were performed with a Perkin–Elmer 240.

stirred for 15 h at room temperature. The solution was reduced in volume and left to crystallise at 3 °C to yield **3b** (yield 82%). In an alternative procedure 70 mg (0.19 mmol) of $[(\text{cod})\text{Rh}(\mu\text{-Dmad})]_2$ [8] were dissolved in 20 ml CH_2Cl_2 . After passage of CO through the solution for 20 min the solvent was removed and **3b** recrystallised as red prisms from ethyl acetate (yield 81%).

3b $[(\text{CO})_2\text{Rh}(\mu\text{-Dmad})]_2$, $\text{C}_{18}\text{H}_{16}\text{N}_{10}\text{O}_4\text{Rh}_2$ (M , 642.2) ^1H NMR (CD_3OD , TMS), 7.75 (s, 2H, Dmad H8), 8.23, 8.24 ppm (2s, 2H, Dmad H2), the Dmad CH_3 -proton signals are masked by the methanol CH_3 -protons.

3c, 94 mg (0.19 mmol) of $[(\text{CO})\text{Rh}(\text{acac})(\text{PPh}_3)]$ were added to 31 mg (0.19 mmol) of N^6, N^6 -dimethyladenine in 10 ml of $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$ to yield an orange solution, which was stirred for 15 h at room temperature. The solvent was removed and **3c** recrystallised from methanol or acetonitrile (yield 78%). In an alternative method 61 mg (0.19 mmol) of **3b** were stirred for 18 h with 48 mg (0.19 mmol) of PPh_3 in 20 ml CH_2Cl_2 ; CO evolution was observed. The solvent was removed and **3c** recrystallised from acetonitrile (yield 81%).

3c $[(\text{CO})\text{Rh}(\mu\text{-Dmad})(\text{PPh}_3)]_2$, $\text{C}_{52}\text{H}_{46}\text{N}_{10}\text{O}_2\text{P}_2\text{Rh}_2$ (M , 1110.8) ^1H NMR (CD_2Cl_2 , TMS), 3.30 (s, br, 12H, Dmad CH_3), 6.77–7.86 (30H, PPh_3 H), 7.79, 7.86 (2s, 2H, Dmad H8), 8.35, 8.45 ppm (2s, 2H, Dmad H2).

Preparation of $[(\text{CO})_2\text{Rh}(\mu\text{-3MadH}_{-1})]_4$ **4**

50 mg (0.19 mmol) of $[(\text{CO})_2\text{Rh}(\text{acac})]$ were added to 28 mg (0.19 mmol) of 3-methyladenine in 10 ml absolute methanol under argon. After stirring for 15 h at room temperature, the yellow solid was isolated by centrifugation then dissolved in a DMSO/methanol mixture and the solution was cooled to –30 °C to yield crystals of **4** (yield 72%).

4 $[(\text{CO})_2\text{Rh}(\mu\text{-3MadH}_{-1})]_4 \cdot (\text{CH}_3)_2\text{SO} \cdot \text{H}_2\text{O}$, $\text{C}_{34}\text{H}_{32}\text{N}_{20}\text{O}_{10}\text{SRh}_4$ (M , 1324.4). ^1H NMR ($\text{DMSO}-d_6$, TMS) 3.85 (s, 12H, 3mad CH_3), 6.78 (s, 4H, 3Mad H6), 7.81 (s, 4H, 3Mad H8), 8.18 ppm (s, 4H, 3Mad H2).

Preparation of $[(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})]_2$ **5**

24 mg (0.045 mmol) of $[(\text{cod})\text{RhCl}]_2$ were added to 14 mg (0.09 mmol) of 8-aza-9-methyladenine in 8 ml methanol under argon. To facilitate the reaction it was necessary to add 0.9 ml of a 0.1 M NaOMe solution. After 10 h stirring at room temperature, the solution was filtered and cooled to 3 °C to yield orange needles of **5** (yield 68%).

5 $[(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})]_2$, $\text{C}_{26}\text{H}_{34}\text{N}_{12}\text{Rh}_2$ (M , 720.4). ^1H NMR (CDCl_3 , TMS), 1.63–3.08 (16H, cod CH_2), 3.33–4.50 (8H, cod CH), 3.96 (s, 6H, Maad CH_3), 5.80 (s, br, 2H, Maad H6), 8.55 ppm (s, 2H, Maad H2).

X-Ray structural analyses of **3c**, **4** and **5**

Suitable crystals of **3c** and **4** were obtained from DMSO/methanol solutions at –30 °C. **3c** crystallised together with one DMSO solvate molecule, **4** with one DMSO and one water solvate molecule (the latter presumably the result of incomplete drying of the methanol used). **5** was crystallised from a methanol solution and contained two molecules of this solvent in the asymmetric unit. Crystal and refinement data are summarized in Table 2. Unit cell constants were obtained from a least-squares fit to the settings of 25 reflections recorded on an Enraf–Nonius CAD4 diffractometer at varied scan rates using Cu-K_α radiation for **3c** and **4** and

Mo- K_α radiation for **5**. Because of the relatively small size of the available crystals of **3c** and **4** Cu- K_α radiation was also employed for the intensity data collection for these complexes. Three monitoring reflections were checked at regular intervals during data collection; no significant decrease in their intensities was observed. The structures were solved by direct methods and refined by full-matrix least-squares. Ring hydrogen atoms for **3c** were included in the refinement at geometrically calculated positions with group isotropic temperature factors. The phenyl rings were refined as regular hexagons with $d(\text{C}-\text{C}) = 1.395 \text{ \AA}$. Anisotropic temperature factors were introduced for the complex Rh, P, O and N atoms. The asymmetric unit of **4** contains a DMSO molecule disordered about a twofold crystallographic symmetry axis and a water molecule lying on this axis. Ring hydrogen atoms for **4** were included in the refinement at calculated positions with group isotropic temperature factors. In view of the limited number of observed reflections (1652 for 155 parameters) only the rhodium atoms were refined anisotropically. Two methanol solvate molecules were located in difference syntheses for the asymmetric unit of **5**. Hydrogen atoms were refined for the base moieties and included at calculated sites for the cod ligands. Group isotropic temperature factors were assigned. With the exception of the methanol atoms all nonhydrogen atoms were refined anisotropically for **5**. Terminal reliability indices are listed in Table 2 where $R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$ with weights given by $w = (\sigma^2(F_o) + p^2 F_o^2)^{-1}$. Final difference syntheses were effectively featureless. Analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion factors are taken from ref. 13. Calculations were performed with SHELX-76 [14] and with local programs. Table 3

Table 2

Crystal and refinement data for **3c**, **4** and **5**

Compound	3c ·DMSO	4 ·DMSO·H ₂ O	5 ·2CH ₃ OH
Empirical formula	C ₅₄ H ₅₂ N ₁₀ O ₃ P ₂ SRh ₂	C ₃₄ H ₃₂ N ₂₀ O ₁₀ SRh ₄	C ₂₈ H ₄₂ N ₁₂ O ₂ Rh ₂
Space group	$P\bar{1}$	$Pbcn$	$P2_1/c$
<i>a</i> (Å)	13.928(5)	13.646(5)	17.456(2)
<i>b</i> (Å)	18.966(10)	24.490(2)	19.802(2)
<i>c</i> (Å)	10.757(4)	14.737(2)	9.221(1)
α (°)	93.46(8)	90	90
β (°)	110.72(5)	90	100.95(1)
γ (°)	96.06(5)	90	90
<i>V</i> (Å ³)	2628(5)	4925(3)	3129(1)
<i>Z</i>	2	4	4
<i>D_c</i> (g cm ⁻³)	1.50	1.79	1.67
Radiation	Cu- K_α	Cu- K_α	Mo- K_α
μ (cm ⁻¹)	65.7	119.2	10.8
Scan type	$\theta-2\theta$	$\theta-2\theta$	ω
$2\theta_{\text{max}}$ (°)	105	110	45
Reflections measured	6336	3271	4105
Reflections observed	2854	1652	3367
Reflection criterion	$F_o^2 < 2\sigma(F_o^2)$	$F_o^2 < 3\sigma(F_o^2)$	$F_o^2 < 3\sigma(F_o^2)$
<i>R</i>	0.075	0.066	0.043
<i>R_w</i>	0.072	0.065	0.044
<i>P</i>	0.022	0.014	0.014

Table 3

Atom positional parameters with equivalent isotropic temperature factors ($\text{\AA}^2 10^3$)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
3c				
Rh(1)	0.1346(1)	0.3020(1)	0.4316(2)	52(1)
Rh(2)	−0.0092(1)	0.2316(1)	0.1363(2)	58(1)
P(1)	0.2635(4)	0.3839(3)	0.4307(5)	53(3)
P(2)	−0.1626(4)	0.2732(3)	0.0975(5)	52(3)
O(10)	0.0132(11)	0.4123(9)	0.4821(17)	98(11)
O(20)	0.0325(11)	0.3185(10)	−0.0649(18)	101(11)
N(11)	−0.0100(14)	0.1647(12)	0.6357(21)	97(13)
N(21)	0.2049(14)	0.0953(11)	0.0887(19)	99(12)
N(13)	0.0313(12)	0.2257(10)	0.4726(19)	81(12)
N(23)	0.1265(12)	0.1828(10)	0.1683(18)	71(11)
N(26)	0.3557(15)	0.0424(11)	0.2256(25)	109(14)
N(16)	−0.1078(15)	0.0447(11)	0.5985(24)	108(15)
N(17)	−0.1214(13)	0.0553(10)	0.3063(22)	89(12)
N(27)	0.3473(10)	0.1496(9)	0.4458(17)	67(10)
N(19)	−0.0413(11)	0.1561(8)	0.2585(18)	54(9)
N(29)	0.2147(11)	0.2183(8)	0.3937(18)	59(9)
S(100)	0.6402(7)	0.8507(6)	0.1114(10)	166(4)
O(100)	0.6083(18)	0.7743(15)	0.1409(25)	208(10)
C(12)	0.0355(19)	0.2179(15)	0.5982(30)	91(9)
C(22)	0.1332(18)	0.1390(14)	0.0695(28)	92(8)
C(24)	0.2011(17)	0.1845(12)	0.2794(26)	64(7)
C(14)	−0.0222(16)	0.1665(12)	0.3879(24)	60(6)
C(15)	−0.0743(17)	0.1025(14)	0.4178(28)	80(7)
C(25)	0.2842(19)	0.1375(14)	0.3125(29)	96(8)
C(26)	0.2817(22)	0.0912(17)	0.2133(31)	109(9)
C(16)	−0.0609(19)	0.1071(16)	0.5483(30)	92(8)
C(28)	0.3029(16)	0.2000(12)	0.4912(23)	71(7)
C(18)	−0.0971(18)	0.0921(15)	0.2130(29)	90(9)
C(10)	0.0627(17)	0.3701(13)	0.4710(23)	77(7)
C(20)	0.0160(19)	0.2841(14)	0.0084(27)	85(9)
C(161)	−0.1641(18)	−0.0193(15)	0.5130(27)	107(9)
C(261)	0.4292(19)	0.0323(14)	0.3525(27)	105(9)
C(262)	0.3381(20)	−0.0040(16)	0.1062(30)	123(10)
C(162)	−0.0856(18)	0.0524(14)	0.7481(29)	105(9)
C(101)	0.5956(19)	0.9128(15)	0.2058(27)	123(10)
C(102)	0.7774(19)	0.8731(15)	0.2069(28)	126(10)
C(112)	0.2431(8)	0.4887(7)	0.2517(13)	63(6)
C(113)	0.2247(8)	0.5563(7)	0.2120(13)	79(7)
C(114)	0.1958(8)	0.6047(7)	0.2905(13)	67(6)
C(115)	0.1853(8)	0.5857(7)	0.4088(13)	75(7)
C(116)	0.2037(8)	0.5182(7)	0.4485(13)	66(6)
C(111)	0.2326(8)	0.4697(7)	0.3700(13)	49(5)
C(122)	0.4498(10)	0.3512(7)	0.4092(10)	68(6)
C(123)	0.5076(10)	0.3255(7)	0.3380(10)	82(7)
C(124)	0.4592(10)	0.3003(7)	0.2031(10)	85(7)
C(125)	0.3529(10)	0.3007(7)	0.1393(10)	82(7)
C(126)	0.2951(10)	0.3264(7)	0.2104(10)	75(7)
C(121)	0.3435(10)	0.3517(7)	0.3454(10)	56(6)
C(132)	0.3537(8)	0.3688(5)	0.7034(14)	61(6)
C(133)	0.4262(8)	0.3864(5)	0.8328(14)	70(6)
C(134)	0.5003(8)	0.4466(5)	0.8614(14)	56(6)
C(135)	0.5020(8)	0.4891(5)	0.7606(14)	62(6)
C(136)	0.4296(8)	0.4715(5)	0.6312(14)	74(7)

Table 3 (continued)

Atom	x	y	z	U_{eq}
3c				
C(131)	0.3554(8)	0.4113(5)	0.6026(14)	50(5)
C(212)	-0.2089(8)	0.2565(6)	0.3252(13)	49(5)
C(213)	-0.2600(8)	0.2228(6)	0.4005(13)	68(6)
C(214)	-0.3402(8)	0.1670(6)	0.3400(13)	93(8)
C(215)	-0.3693(8)	0.1448(6)	0.2042(13)	94(8)
C(216)	-0.3182(8)	0.1785(6)	0.1289(13)	87(8)
C(211)	-0.2380(8)	0.2343(6)	0.1894(13)	50(5)
C(222)	-0.2440(8)	0.3957(7)	0.1566(13)	61(6)
C(223)	-0.2430(8)	0.4691(7)	0.1775(13)	71(7)
C(224)	-0.1580(8)	0.5159(7)	0.1797(13)	86(8)
C(225)	-0.0739(8)	0.4892(7)	0.1611(13)	79(7)
C(226)	-0.0749(8)	0.4158(7)	0.1402(13)	66(6)
C(221)	-0.1600(8)	0.3690(7)	0.1380(13)	50(5)
C(232)	-0.2255(7)	0.2041(6)	-0.1561(13)	60(6)
C(233)	-0.2943(7)	0.1827(6)	-0.2863(13)	77(7)
C(234)	-0.3878(7)	0.2106(6)	-0.3350(13)	73(7)
C(235)	-0.4124(7)	0.2600(6)	-0.2534(13)	68(6)
C(236)	-0.3435(7)	0.2814(6)	-0.1231(13)	60(6)
C(231)	-0.2501(7)	0.2535(6)	-0.0745(13)	42(5)
4				
Rh(1)	0.6721(1)	0.0936(1)	0.0951(1)	51(1)
Rh(2)	0.6720(1)	0.1703(1)	0.4181(1)	52(1)
S(50)	0.5071(9)	0.2245(5)	0.7152(8)	89(4)
O(10)	0.8840(12)	0.1170(6)	0.1087(11)	83(5)
O(20)	0.7331(12)	-0.0233(6)	0.1161(10)	83(5)
O(30)	0.6810(14)	0.1443(6)	0.6124(12)	106(6)
O(40)	0.6496(11)	0.2861(6)	0.4744(10)	78(5)
O(50)	0.5000	0.1722(7)	0.7500	144(11)
O(60)	0.4395(26)	0.4478(12)	0.2216(23)	114(13)
N(11)	0.5081(12)	-0.0096(6)	0.1256(11)	52(4)
N(21)	0.6346(12)	0.2703(6)	0.2667(11)	60(5)
N(13)	0.3536(13)	-0.0501(6)	0.1549(11)	54(5)
N(23)	0.5936(12)	0.3129(6)	0.1242(11)	56(5)
N(16)	0.5264(11)	0.0840(5)	0.0946(10)	44(4)
N(26)	0.6635(12)	0.1785(5)	0.2841(9)	43(4)
N(17)	0.3006(12)	0.0890(6)	0.1124(11)	56(5)
N(27)	0.6344(10)	0.1761(5)	0.0736(10)	39(4)
N(19)	0.2145(13)	0.0123(7)	0.1474(12)	68(6)
N(29)	0.5915(13)	0.2515(7)	-0.0028(13)	63(5)
C(22)	0.6084(15)	0.3132(8)	0.2138(15)	61(7)
C(12)	0.4515(16)	-0.0501(8)	0.1472(14)	56(6)
C(23)	0.5642(17)	0.3636(8)	0.0696(16)	73(7)
C(13)	0.2908(16)	-0.0987(8)	0.1801(14)	61(6)
C(24)	0.6062(14)	0.2636(7)	0.0884(13)	51(5)
C(14)	0.3108(14)	-0.0023(8)	0.1395(13)	50(5)
C(15)	0.3641(15)	0.0447(8)	0.1179(13)	53(6)
C(25)	0.6350(14)	0.2180(7)	0.1333(13)	42(5)
C(26)	0.6464(13)	0.2198(7)	0.2298(13)	43(5)
C(16)	0.4685(14)	0.0419(7)	0.1103(13)	48(5)
C(18)	0.2117(16)	0.0677(8)	0.1297(13)	54(6)
C(28)	0.6106(16)	0.1957(7)	-0.0105(13)	65(7)
C(10)	0.8037(15)	0.1054(8)	0.0980(15)	55(6)
C(20)	0.7026(16)	0.0215(9)	0.1092(15)	72(7)
C(30)	0.6747(17)	0.1587(7)	0.5379(14)	51(5)
C(40)	0.6581(16)	0.2409(8)	0.4450(14)	63(6)
C(50)	0.3974(13)	0.2652(9)	0.7356(18)	117(10)

Table 3 (continued)

Atom	x	y	z	U_{eq}
5				
Rh(1)	0.1865(1)	0.9824(1)	0.2124(1)	33(1)
Rh(2)	0.2650(1)	1.0714(1)	−0.0117(1)	32(1)
N(11)	0.3062(3)	0.9538(3)	0.2526(6)	34(3)
N(21)	0.2733(3)	0.9703(3)	−0.0849(6)	34(3)
N(13)	0.3879(4)	0.8658(3)	0.3801(7)	45(4)
N(23)	0.3421(4)	0.9052(3)	−0.2370(7)	44(4)
N(16)	0.3552(3)	1.0521(3)	0.1646(6)	36(3)
N(26)	0.1704(4)	0.9292(3)	0.0171(6)	42(4)
N(17)	0.5151(4)	0.9948(4)	0.3099(7)	52(4)
N(27)	0.1893(4)	0.8028(3)	−0.1669(7)	51(4)
N(28)	0.2229(4)	0.7614(3)	−0.2482(8)	56(4)
N(18)	0.5650(4)	0.9513(4)	0.3807(8)	58(4)
N(29)	0.2836(4)	0.7945(3)	−0.2856(7)	43(4)
N(19)	0.5239(4)	0.8981(3)	0.4168(7)	48(4)
C(12)	0.3209(4)	0.8939(4)	0.3199(8)	42(4)
C(22)	0.3285(5)	0.9589(4)	−0.1640(9)	43(4)
C(14)	0.4474(4)	0.9088(4)	0.3687(8)	38(4)
C(24)	0.2881(4)	0.8570(4)	−0.2282(7)	36(4)
C(15)	0.4419(4)	0.9693(4)	0.3027(7)	34(4)
C(25)	0.2289(4)	0.8617(3)	−0.1522(7)	34(4)
C(16)	0.3674(4)	0.9952(3)	0.2372(7)	32(4)
C(26)	0.2214(4)	0.9213(4)	−0.0701(7)	33(4)
C(29)	0.3349(6)	0.7614(4)	−0.3691(10)	59(5)
C(19)	0.5639(6)	0.8423(5)	0.4982(11)	74(6)
C(111)	0.0716(4)	1.0209(4)	0.1765(9)	49(5)
C(112)	0.0720(4)	0.9536(4)	0.2213(9)	49(5)
C(113)	0.0673(6)	0.9318(5)	0.3739(10)	73(6)
C(114)	0.1234(6)	0.9634(5)	0.4930(9)	68(6)
C(115)	0.1974(5)	0.9906(4)	0.4431(8)	51(5)
C(116)	0.2017(5)	1.0540(4)	0.3870(8)	48(5)
C(117)	0.1348(5)	1.1043(4)	0.3674(10)	61(5)
C(118)	0.0606(5)	1.0798(5)	0.2759(11)	70(6)
C(221)	0.2364(5)	1.1659(4)	0.0709(9)	51(5)
C(222)	0.3009(5)	1.1731(4)	0.0026(8)	48(5)
C(223)	0.2966(6)	1.2037(5)	−0.1470(10)	81(6)
C(224)	0.2525(7)	1.1650(5)	−0.2717(9)	84(7)
C(225)	0.2220(5)	1.0969(4)	−0.2353(8)	52(5)
C(226)	0.1599(5)	1.0886(4)	−0.1661(9)	52(5)
C(227)	0.1138(5)	1.1471(5)	−0.1191(12)	81(7)
C(228)	0.1552(6)	1.1892(5)	−0.0002(11)	77(6)
O(311)	0.4993(4)	0.3586(3)	0.6438(7)	75(2)
O(411)	0.0506(7)	0.7069(7)	0.4616(14)	192(5)
C(311)	0.5070(8)	0.3624(7)	0.4941(16)	129(5)
C(411)	0.0386(8)	0.7597(8)	0.5352(15)	115(4)

contains the atom positions parameters and equivalent isotropic temperature factors for **3c**, **4** and **5**.

Discussion

The X-ray structural analysis of **3c** establishes a dimeric structure for this complex with N3,N9-coordination as depicted in Fig. 1. As **3c** may be prepared

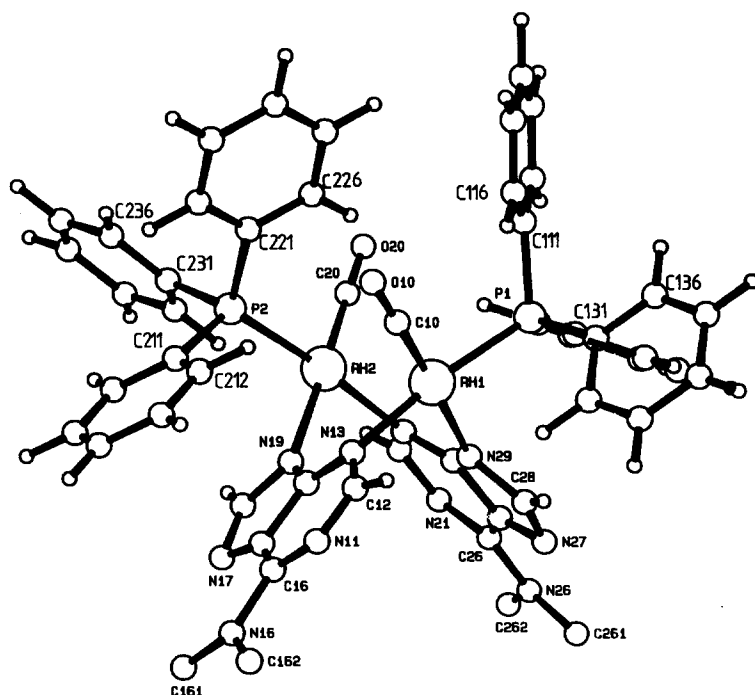


Fig. 1. Molecular structure of $[(\text{CO})\text{Rh}(\mu\text{-Dmad})(\text{PPh}_3)]_2$ **3c**.

directly by ligand substitution from **3b** $[(\text{CO})_2\text{Rh}(\mu\text{-Dmad})]_2$ and $[(\text{cod})\text{Rh}(\mu\text{-Dmad})]_2$ [8] it may safely be concluded that these complexes also display similar dimeric structures. The PPh_3 ligands in **3c** are both sited *trans* to pyrimidine nitrogen atoms $\text{N}x3$ ($x = 1, 2$), the carbonyl ligands *trans* to imidazole nitrogens $\text{N}x9$ ($x = 2, 1$). In principle the complex should be capable of exhibiting an approximately C_2 symmetry. However, although analogous bond distances to the respective rhodium atoms do, indeed, display similar values, this is not the case for the bond angles. Marked distortions from a perfect square planar geometry are observed. In particular $\text{N}23\text{-Rh}2\text{-N}19$ [$84.2(6)^\circ$] is 5.0° narrower than the analogous bond angle $\text{N}13\text{-Rh}1\text{-N}29$ [$89.2(7)^\circ$]; $\text{N}23\text{-Rh}2\text{-C}20$ [$91.7(9)^\circ$] is 4.3° wider than $\text{N}13\text{-Rh}1\text{-C}10$ [$87.4(9)^\circ$]. These distortions are also retained in solution, as evidenced by the appearance of separate signals for each of the ring protons $\text{H}12/\text{H}22$ (δ 8.35, 8.45) and $\text{H}18/\text{H}28$ (δ 7.79, 7.86) in the ^1H NMR spectrum taken in CD_2Cl_2 solution.

It seems reasonable to assume that the magnitude of these angular deviations from the idealised square planar geometry is a result of steric interactions between the bulky PPh_3 ligands and the purine bases. Supporting evidence for this hypothesis is provided by the ^1H NMR spectra of $[(\text{cod})_2\text{Rh}(\mu\text{-Dmad})]_2$, **3a** and **3b**. In the former complex, which contains the relatively bulky cod ligands, a marked non-equivalence of the ring protons $\text{H}2$ and $\text{H}8$ in the two Dmad ligands is observed.

Signals appear at δ 8.33/8.45 for the $\text{H}2$ protons and δ 7.82/7.90 for the $\text{H}8$ protons. The less bulky nbd ligands lead to markedly less pronounced differences in the chemical shifts for the non-equivalent $\text{H}2$ and $\text{H}8$ protons in $[(\text{nbd})_2\text{Rh}(\mu\text{-Dmad})]_2$.

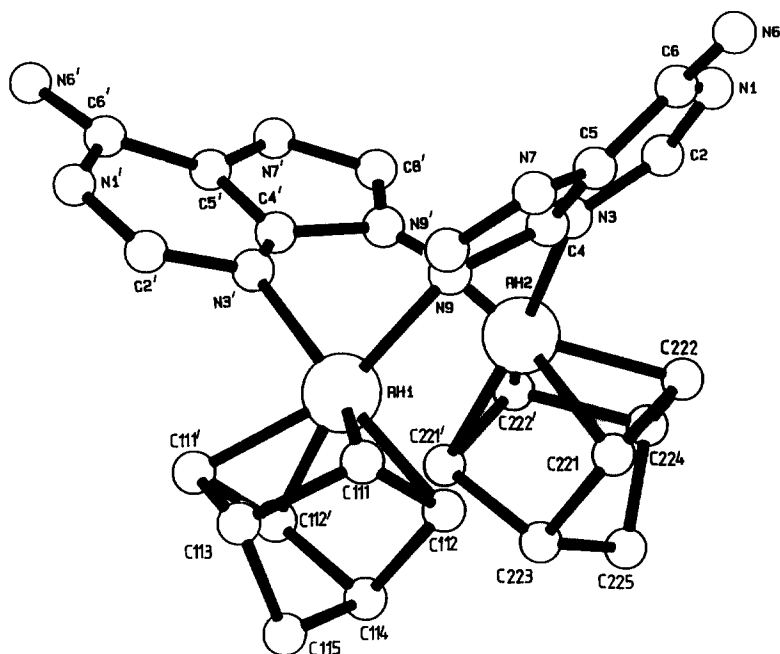


Fig. 2. Molecular structure of $[(nbd)Rh(\mu\text{-Ad})]_2$ **1**.

Dmad)]₂ **3a**. Values of 8.17/8.20 and 7.67/7.68 for the H2 and H8 protons, respectively, were recorded. For **3b** $[(CO)_2Rh(\mu\text{-Dmad})]_2$ a splitting of the H8 signals (δ 7.75 ppm) is no longer apparent and that for the H2 signals (δ 8.23, 8.24 ppm) is marginal. The Rh1...Rh2 distance is 3.210(1) Å in **3c**, which is 0.09 Å longer than that in $[(CO)_2RhCl]_2$ [15]. Such separations have often been considered as providing evidence for a degree of metal-metal interaction in binuclear rhodium(I) complexes. The rhodium coordination planes are inclined at an angle of 43.4° to one another and make respective angles of 67.1° and 69.3° with the Rh1...Rh2 vector.

For steric reasons, as a consequence of the dimethylation of N6 the pyrimidine nitrogen N1 and the imidazole nitrogen N7 are not available as coordination sites in DmadH. For adenine itself or for *N*⁶-methyladenine these sites should be capable of competing with N3, so that N9,N1 or N9,N7 binding pairs should be feasible. We have, indeed, observed the latter combination in the arene-ruthenium(II) complex $[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{AdH})]_4\text{Cl}_4$ [16]. Crystals of **1** with dimensions (0.40 × 0.15 × 0.10 mm) suitable for X-ray structural analysis were grown from an acetone solution, but on exposure to X-rays (Cu-*K*α-radiation) these rapidly lost acetone solvate molecules so that we could collect only a partial intensity data set for this complex, but this was adequate to confirm N3,N9-coordination in a dimeric structure [17*] as depicted in Fig. 2. As for the analogous Dmad derivative **3a**, separate signals are observed for the independent H2 protons (δ 8.17, 8.21) in the ¹H NMR spectrum of

* A reference number with an asterisk indicates a note in the list of references.

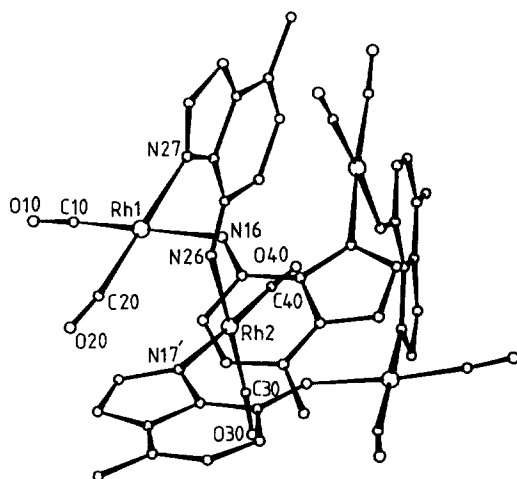


Fig. 3. Molecular structure of $[(\text{CO})_2\text{Rh}(\mu\text{-3madH}_{-1})]_4$ **4**.

1 taken in $\text{DMSO-}d_6$. A similar phenomenon is observed for the independent H2 and H8 signals in the 6Mad complexes **2a** and **2b**, and so it may reasonably be assumed that these also exhibit a dimeric structure with N3,N9-coordination.

This binding mode is no longer possible for 3-methyladenine (3mad). Alkylation of endocyclic heteroatoms of adenine can often lead to pronounced changes in metal-binding properties. The imidazole nitrogen N7 has been established as the primary metal binding site in a number of 3-alkylated adenine metal complexes [18–20]. In a systematic study of the interaction of the $\text{CH}_3\text{Hg(II)}$ cation with 3mad we were also able to isolate and characterize complexes with N6 and N9 as secondary binding sites [21]. N1 coordination of 3mad has not been observed.

As depicted in Fig. 3, **4** displays a tetrameric structure with N6,N7-coordination. The molecule displays crystallographic C_2 -symmetry with the $\text{Rh}_x\text{-N}_x6$ ($x = 1, 2$) bonds adopting a *cis*-position relative to the $\text{N}_x1\text{-C}_x6$ bond. Dimer formation would require these $\text{Rh}_x\text{-N}_x6$ bonds to adopt the alternative *trans*-position and lead to unreasonably short steric contacts between the ligands of the square planar rhodium coordination spheres. Geometrically calculated positions for the amino protons H16 and H26 indicate that these approach the rhodium atoms Rh2 and Rh1 at distances $\text{Rh}_x \cdots \text{Hy}6$ ($x = 2, y = 1$; $x = 1, y = 2$) of 2.62 and 2.59 Å, with angles between the $\text{Rh}_x \cdots \text{Hy}6$ interactions and the Rh_x coordination planes of respectively 71.3 and 71.2°. This interaction leads to a marked highfield shift for the amino proton in the ^1H NMR spectrum of **4** (6.78 ppm) in comparison to the free base (7.76 ppm, $\text{DMSO-}d_6$). The rhodium coordination planes are inclined at angles of 99.6 and 87.0°, respectively, to the base planes containing N_x7 ($x = 2$ and 1, respectively).

In contrast to 3-methyladenine, N1 and N7 compete as primary binding sites in 9-alkyl-adenine derivatives and in adenosine [22]. Because N1,N6-coordination allows dimer formation, as evidenced by $[(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})\text{Rh}(\text{cod})\text{Cl}]_2$ [8], this binding mode might be expected to offer an attractive alternative for such bases to the N6,N7-combination observed in **4**. Unfortunately we have been unable to prepare and characterize complexes of 9-ethyladenine 9Etad of the type $[\text{L}_2\text{Rh}(\mu\text{-}$

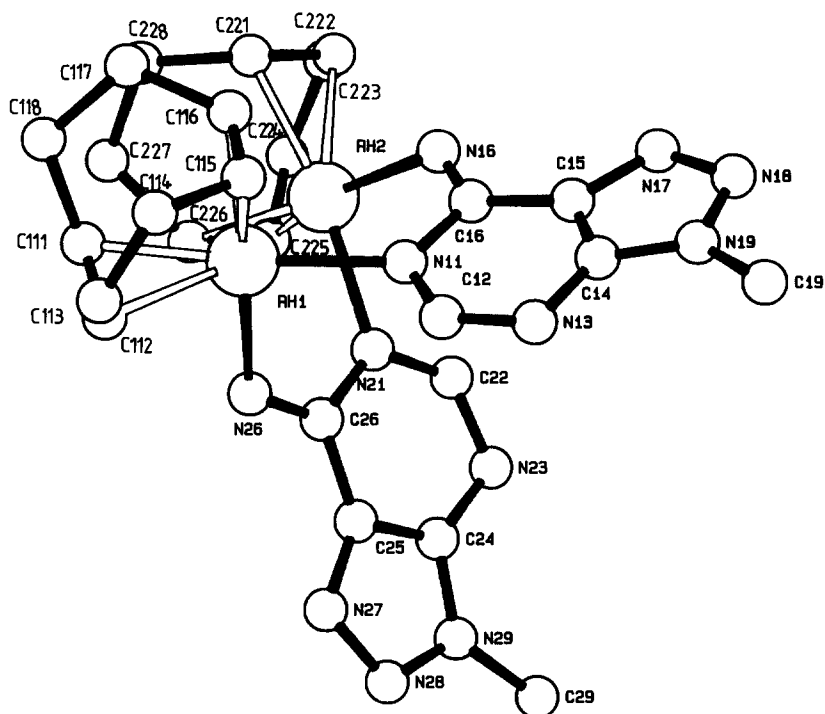


Fig. 4. Molecular structure of $[(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})]_2$ **5**.

9Etad)]_n ($L_2 = \text{cod}$, nbd or $(\text{CO})_2$; $n = 2, 4$). Our studies involving Etad with complexes $[\text{L}_2\text{Rh}(\text{acac})]$ in various solvents indicate that no products of the above type may be isolated. As N1,N6-binding should lead to isolable dimers, this suggests that this binding mode is not favoured for 9-alkyl-adenine derivatives.

We have, however, been able to structurally characterize a further cod complex of 8-aza-9-methyladenine, namely $[(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})]_2$ **5**, the molecular structure of which is depicted in Fig. 4. Replacement of the 8-CH groups in purine bases by an aza nitrogen leads to pronounced withdrawal of electron density from both of the adjacent nitrogens N7 and N9. If N9 is bonded to either an alkyl group, a proton, or a metal ion, then either N1 or N3 of the pyrimidine ring should be the chosen metal binding site [6,23]. The N1,N6-binding mode for the bridging MaadH_{-1} ligands in **5** is in accordance with this prediction.

Bond lengths and angles to the rhodium atoms in **5** are similar to those in $[(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})\text{Rh}(\text{cod})\text{Cl}]_2$ [8]. As in **4**, the $\text{Rh}-\text{N}_x6$ ($x = 1, 2$) distances are markedly shorter than those to N_x7 (average values 1.99 and 2.09 in **4**, 2.071 and 2.127 Å in **5**). In **3c** no significant difference was observed between the $\text{Rh}-\text{N}_x3$ and $\text{Rh}-\text{N}_x9$ ($x = 1, 2$) bond lengths [range 2.11(2)–2.13(2) Å]. The $\text{Rh1} \cdots \text{Rh2}$ distance of 3.213(1) Å in **5** is very similar to that of 3.210(1) Å in **3c** and 3.255(1) Å in $[(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})\text{Rh}(\text{cod})\text{Cl}]_2$. Striking differences can be seen between the central eight-membered ring in **5** and that in the latter complex. In $[(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})\text{Rh}(\text{cod})\text{Cl}]_2$ the symmetry-related rhodium atoms bonded to N1 are displaced by 1.08 Å from the plane of the heterocycle containing this atom, leading to an angle of 28.9° between this base plane and the $\text{Rh}-\text{N1}$ bond. These rhodium

Table 4

Bond distances (Å) and angles (°) to the rhodium atoms

3c			
Rh1–P1	2.251(6)	Rh2–P2	2.264(5)
Rh1–N13	2.11(2)	Rh2–N23	2.12(2)
Rh1–N29	2.13(2)	Rh2–N19	2.12(2)
Rh1–C10	1.83(2)	Rh2–C20	1.85(3)
P1–Rh1–N13	168.8(5)	P2–Rh2–N23	174.5(5)
P1–Rh1–N29	90.5(7)	P2–Rh2–N19	92.1(4)
P1–Rh1–C10	92.5(7)	P2–Rh2–C20	91.2(8)
N13–Rh1–N29	89.2(7)	N23–Rh2–N19	84.2(6)
N13–Rh1–C10	87.4(9)	N23–Rh2–C20	91.7(9)
N29–Rh1–C10	176.3(9)	N19–Rh2–C20	170.1(9)
4			
Rh1–N16	2.003(15)	Rh2–N26	1.987(14)
Rh1–N27	2.108(13)	Rh2–N17 ^a	2.074(14)
Rh1–C10	1.82(2)	Rh2–C30	1.79(2)
Rh1–C20	1.83(2)	Rh2–C40	1.78(2)
N16–Rh1–N27	82.5(5)	N26–Rh2–N17 ^a	83.8(5)
N16–Rh1–C10	177.4(7)	N26–Rh2–C30	176.0(7)
N16–Rh1–C20	96.5(8)	N26–Rh2–C40	96.7(7)
N27–Rh1–C10	95.3(7)	N17 ^a –Rh2–C30	93.3(7)
N27–Rh1–C20	177.6(8)	N17 ^a –Rh2–C40	175.8(8)
C10–Rh1–C20	87.7(7)	C30–Rh2–C40	86.4(8)
5			
Rh1–N11	2.128(6)	Rh2–N21	2.126(6)
Rh1–N26	2.069(6)	Rh2–N16	2.073(5)
Rh1–C111	2.113(8)	Rh2–C221	2.116(7)
Rh1–C112	2.096(7)	Rh2–C222	2.106(7)
Rh1–C115	2.106(7)	Rh2–C225	2.117(7)
Rh1–C116	2.123(7)	Rh2–C226	2.125(8)
N11–Rh1–N26	88.9(2)	N21–Rh2–N16	89.3(2)
N11–Rh1–C111	174.2(3)	N21–Rh2–C221	169.2(3)
N11–Rh1–C115	87.0(3)	N21–Rh2–C225	87.1(3)
N26–Rh1–C111	94.7(3)	N16–Rh2–C221	94.4(3)
N26–Rh1–C115	152.9(3)	N16–Rh2–C225	152.1(3)
C111–Rh1–C115	91.8(3)	C221–Rh2–C225	94.3(3)

^a Symmetry position *a*: 1 – *x*, *y*, $\frac{1}{2}$ – *z*.

atoms lie at a distance of -0.16 Å from the plane of the second heterocycle, which contains the binding amino nitrogens N6. This state of affairs is effectively summarised by the torsion angles: Rh–N1–C6–N6 -34.0° ; N1–C6–N6–Rh -13.0° . In contrast, the following torsion angles were obtained for **5**: Rh1–N11–C16–N16 -15.4 , Rh2–N21–C26–N26 -14.2 , N11–C16–N16–Rh2 -30.6 , N21–C26–N26–Rh1 -31.9° . Rh1 is displaced by respectively 0.41 Å (N11 plane) and 1.17 Å (N26 plane), Rh2 by -0.31 (N21 plane) and -1.00 Å (N16 plane) from the heterocycle planes. Twisting of the bonds N16–C16 and N26–C26 relative to the 8-azaadenine planes in **5** leads to a marked reduction in the degree of π -delocalisation possible for the amino nitrogen p_z orbitals. This state of affairs is underlined by the dramatic highfield shift of the amino proton from δ 8.81 in [(cod)Rh(μ -MaadH $_{-1}$)Rh(cod)Cl] $_2$

Table 5

¹H NMR parameters for the cod ligands ^a in [(cod)Rh(μ-MaadH₁)₂ **5** (in CDCl₃)

Proton	δ (ppm)	Proton	δ (ppm)
olefinic protons ^a		methylene protons ^a	
H _{xx} 2	4.50	H _{xx} 7	3.08
H _{xx} 1	4.35	H _{xx} 3	2.80
H _{xx} 6	4.25	H _{xx} 8	2.60
H _{xx} 5	3.33	H _{xx} 3'	2.20
		H _{xx} 7'	2.20
		H _{xx} 4	2.20
		H _{xx} 8'	1.80
		H _{xx} 4'	1.63

^a _{xx} = 11 or 22.

to δ 5.80 in **5**. At the same time the C2 proton is shifted to lower field from δ 8.21 to δ 8.55.

A complete assignment of the ¹H NMR spectrum of [(cod)Rh(μ-MaadH₁)₂ **5** was carried out by NOE and two-dimensional NMR techniques. As may be seen from Fig. 4 the cod ligands adopt the characteristic boat conformation. C₂-symmetry and, therefore, equivalence of the cod ligands, may be assumed for solution. The numbering scheme for the ring hydrogen atoms (e.g. H221 is bonded to C221) is given in Fig. 5. In the solid state close interatomic distances of less than 2.5 Å are observed between the following base and cod protons:

N(16)H ⋯ H112

N(26)H ⋯ H222

(C12)H ⋯ H115

C(22)H ⋯ H225

An appreciable NOE effect was established for the following MaadH₁-cod resonance pairs (*x* = 1, 2)

δ (N_x6)H 5.80–H_{xx}2 4.50

δ (C_x2)H 8.55–H_{xx}5 3.33

With this information from the NOESY spectrum it is possible to assign all cod protons as listed in Table 5. In accordance with the results of Rodman and Mann for [Ir(cod)(μ-hp)]₂ (hp = 2-hydroxypyridinate) [24] it was assumed that the *endo* (designated with the symbol ') methylene protons resonate upfield of the *exo* methylene protons. Figure 5 shows the cod region of the COSY spectrum.

Our results indicate that the N3,N9 binding mode will be preferred by the bridging adeninate ligands Ad, 6Mad and Dmad in diene-rhodium(I) complexes. When N9 is blocked or sterically unavailable then N6 may be metallated. The observation of either N6,N1 or N6,N7 coordination will be influenced by the metal binding proclivity of the pyrimidine and imidazole ring nitrogens N1 and N7. The former binding mode requires significant displacement of the rhodium atoms from either the plane of the coordinated N1 atom or that of the metallated N6 atom. It is observed for 8-aza-9-methyladenine, for which N7 has a relatively low electron density. The N6,N7 binding mode will presumably be preferred by adenine nucleosides. Interestingly this coordination pattern is available for adenine moieties in DNA even when they participate in Watson-Crick base-pairing. It thus seems probable that the antitumour derivative [(cod)Rh(acac)] will preferentially bind

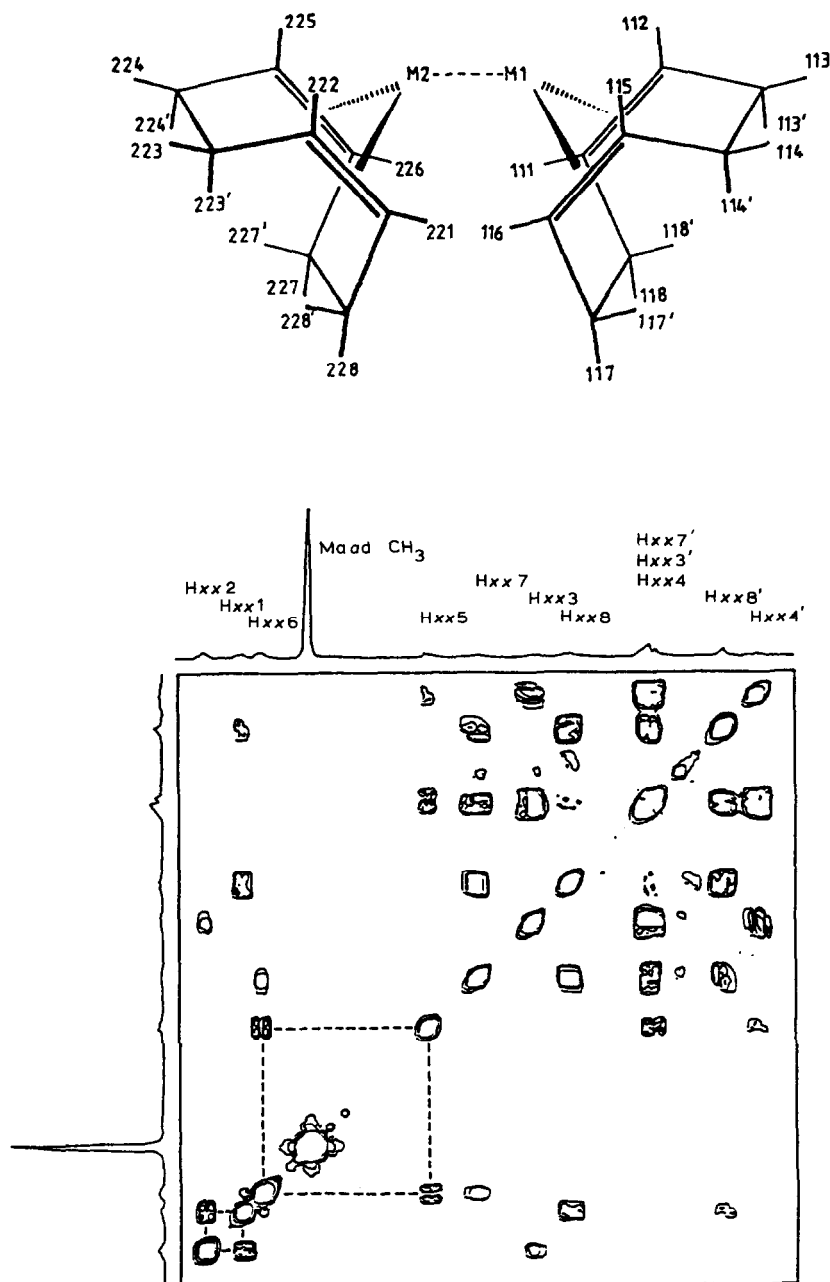


Fig. 5. COSY spectrum of $[(\text{cod})\text{Rh}(\mu\text{-MaadH}_{-1})_2]_2$ 5, cod region.

adenines rather than guanines in DNA, as has been observed for *cis*-platinum(II) complexes. In a forthcoming paper we will report on our investigations on the reaction between $[(\text{cod})\text{Rh}(\text{acac})]$ and pyrimidine bases.

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