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# Pentacoordinated diolefinic rhodium(I) organocomplexes with α-diimine ligands. Crystal structures of $[Rh(Nbd)(LL)(PPh_3)]ClO_4$ (Nbd = norbornadiene; LL = Bdh, biacetylidihydrazone; Pvdh, pyruvaldihydrazone; Bda, biacetyldianil)

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## Abstract

Pentacoordinated $[Rh(Nbd)(LL)(PPh_3)]ClO_4$ (Nbd = norbornadiene; LL = biacetyldihydrazone (Bdh) (**1**), pyruvaldehydedihydrazone (Pvdh) (**2**), glyoxaldihydrazone (Gdh) (**3**), biacetyldianyl (Bda) (**4**)) complexes are studied. The molecular structures of **1**, **2**, and **4** have been determined by X-ray diffraction. The three cations are best described as having distorted trigonal bipyramidal geometry with the olefinic bonds of Nbd spanning axial–equatorial sites; in **1** and **2** the other equatorial positions are occupied by the diimine groups and the $PPh_3$ is in axial position while in **4** the diimine occupies axial–equatorial sites and the $PPh_3$ is in equatorial position. Complexes **1** and **2** show intermolecular hydrogen bond $N–H\cdots OClO_3$ linkages, strong in **2**. In acetone solution compounds **1**–**4** undergo phosphine dissociation, inhibited at 273 K; **2**, **3** and **4** behave as dimers with bridging diimine ligands. Neutral pentacoordinated $[Rh(X)(L_2)(LL)]$ (X = Cl, $SnCl_3$; $L_2$ = Nbd, 1,5-cyclooctadiene (Cod); LL = Pvdh, Gdh) compounds undergo ionic dissociation in solution where at 183 K $[Rh(SnCl_3)(Nbd)(Pvdh)]$ shows a square pyramidal structure with $SnCl_3$ in apical position. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Rhodium complexes; Pentacoordinated complexes; Diimine complexes; Crystal structures; Trichlorostannate

## 1. Introduction

Five-coordinated compounds may adopt trigonal bipyramidal (tbp) or square pyramidal (sp) geometry and both types of structures are well known for pentacoordinated rhodium(I) complexes [1–9]. Recently the crystal structures of pentacoordinated [Rh(Cl)(Nbd)-(py-2-CH=NR)] [10] and $[Rh(Nbd)(RN{=}C(H)C(H){=}N–R)(PPh_3)]BF_4$ (R = $4-Me_2N–C_6H_4$, (Gaa)) [11] have been reported and both compounds show a tbp structure where the diolefin occupies the usual equatorial–axial disposition because of chelate strain [5,12–14] and the N-donor ligands occupy equatorial sites. It is well known that in $d^8$ metal complexes adopting a tbp geometry σ-donor ligands prefer axial sites, while the strongest π-acceptor ligands lie in equatorial positions where the largest extent of π-back-donation is expected [15]. α-Diimines behave as σ-donor and π-acceptor ligands [16], therefore occupancy of equatorial–equatorial or axial–equatorial sites in a tbp can be expected. Biacetyl derivatives show a lower π-acceptor capability than glyoxal derivatives [17] and may also show repulsive interaction between the methyl groups when adopting the *cis*-chelating coordination [18]. Provided the other ligands are the same, the disposition adopted for a particular α-diimine should depend on its relative σ-donor/π-acceptor capability but also on steric requirements [19], therefore we thought it interesting to

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study $[Rh(Nbd)(LL)(PPh_3)]ClO_4$ complexes containing diimines (LL) with different electronic and steric properties. The ligands used were dihydrazones $H_2N–N=C(R')–C(R'')=N–NH_2$ derived from glyoxal (R′=R″=H; Gdh), pyruvaldehyde (R′=$CH_3$, R″=H; Pvdh) or biacetyl (R′=R″=$CH_3$; Bdh) and the biacetyl derivative $(C_6H_5)N=C(CH_3)C(CH_3)C=N(C_6H_5)$ (Bda). Dihydrazones show, according to the absorptions in the electronic spectra of $Mo(CO)_4$(diimine) complexes, enhanced donor properties due to the presence of the $NH_2$ group [20] and low steric requirements. Bda, being an aryl *N*-substituted diimine, shows enhanced π-acceptor capability [17] and higher steric requirements. On the other hand neutral pentacoordinated complexes [Rh(X)(Nbd)(LL)] with LL = 2,2′-bipyridine (X = Cl) [2] or glyoxalbis(cyclohexylimine) (X = $SnCl_3$) [21] adopt distorted sp geometry with the anionic group in apical position, therefore neutral pentacoordinated diolefinic compounds containing Gdh or Pvdh have also been studied.

## 2. Results and discussion

Cationic pentacoordinated $[Rh(Nbd)(LL)(PPh_3)]ClO_4$ (LL = Bdh, **1**; Pvdh, **2**; Gdh, **3** or Bda, **4**) complexes are readily obtained by the reaction of $[\{Rh(Nbd)Cl\}_2]$ with triphenylphosphine and $AgClO_4$ in acetone solution ($Rh–PPh_3–ClO_4$ = 1:1:1) followed by the addition of the corresponding α-diimine, (Rh–LL = 1:1). IR spectra of **1**–**4** show the expected bands for coordinated diimine ligands and in the complexes containing dihydrazones (**1**–**3**) the absorptions due to ν(N–H) are not displaced towards lower frequencies with respect to the free ligands, though the appearance of several bands in this region [22] and the splitting of ν(Cl–O) in **2** and **3** suggest the existence of hydrogen bonding between the amino groups and the $ClO_4$ anion.

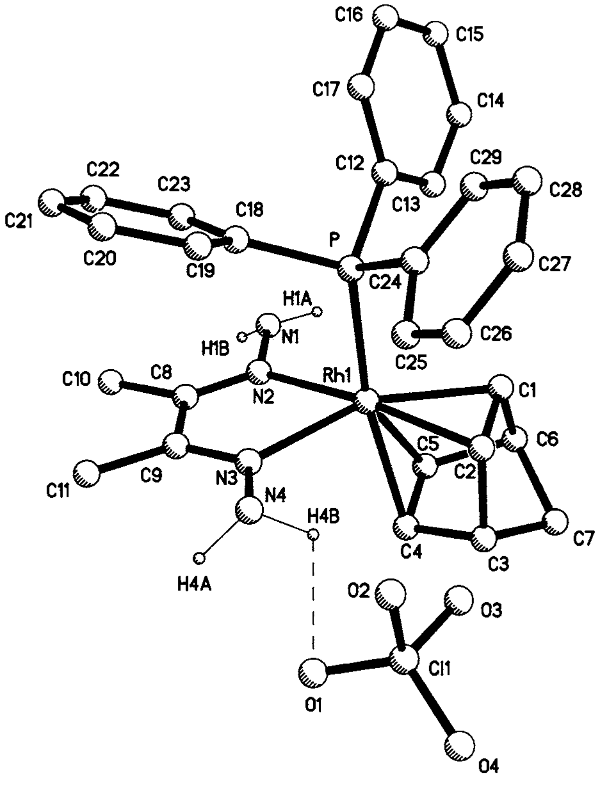

Fig. 1. PLUTO view of **1** showing the atomic numbering. The solvent molecule and the hydrogen atoms have been omitted for clarity.

The molecular structures of compounds **1**, **2** and **4** are shown in Figs. 1–3, respectively. Complex **1** crystallises as $[Rh(Nbd)(Bdh)(PPh_3)]ClO_4 \cdot 1/2CH_2Cl_2$. Crystal data are collected in Table 1. Single crystals of compound **3** could not be obtained due to decomposition. The crystals consist of $[Rh(Nbd)(LL)(PPh_3)]^+$ cations and $ClO_4^-$ anions in all cases. In both **1** and **2** anions and cations are bonded through hydrogen bonds (Table 2). The molecular geometry in the three cases can be best described as a distorted tbp, as can be deduced from a careful study of the selected bond distances and angles, which are given in Table 3. In dihydrazone compounds **1** and **2**, the disposition of the ligands around the rhodium atom is analogous to that found in the related $[Rh(Nbd)(Gaa)(PPh_3)]^+$ [11]. The equatorial plane is occupied by both imino N atoms of the LL ligand and one of the olefinic bonds C1122 of the Nbd group, the other olefinic bond C4455 and the P atom of the $PPh_3$ ligand being in axial positions. C1122 and C4455 are the midpoints of the olefinic bonds in the Nbd group. In both compounds the rhodium atom deviates 0.144(1) Å for **1** and 0.132(1) Å for **2** from the N2N3C1122 plane [23]. This equatorial plane forms a dihedral angle of 86.9(7) and 88.2(5)° with the C4455RhP plane, and of 54.1(3) and 53.8(4)° with the plane containing the diolefinic carbon atoms of the Nbd group, C1C2C4C5, in **1** and **2** respectively. These facts together with the shorter Rh–C1122 distance with respect to the Rh–C4455 distance, due to stronger π-back-bonding in the equatorial plane [10,15], confirm the distorted tbp geometry. The C8–C9 distance in the diimine ligand is longer for **1** (1.46(2) Å) than for **2** (1.40(2) Å), and this difference can be due to the repulsive interaction between the two methyl groups bonded to the carbon atoms of the diimine in **1** [18]. Also, in compound **2** the two Rh–N distances are equal (2.20(1) Å) whilst in **1** they are different (2.224(4) and 2.168(7) Å). In **2** only the amino group bonded to the N=CH group is involved and forms two hydrogen bonds, a strong bond with one oxygen atom of the perchlorate group in the same asymmetric unit, N4–H4A···O1, and a weak bond with another perchlorate group, N4–H4B···O3′ [22]. This feature leads to the formation of ‘dimer units’ as depicted in Fig. 4. In **1** the two amino groups have a weak hydrogen bond each

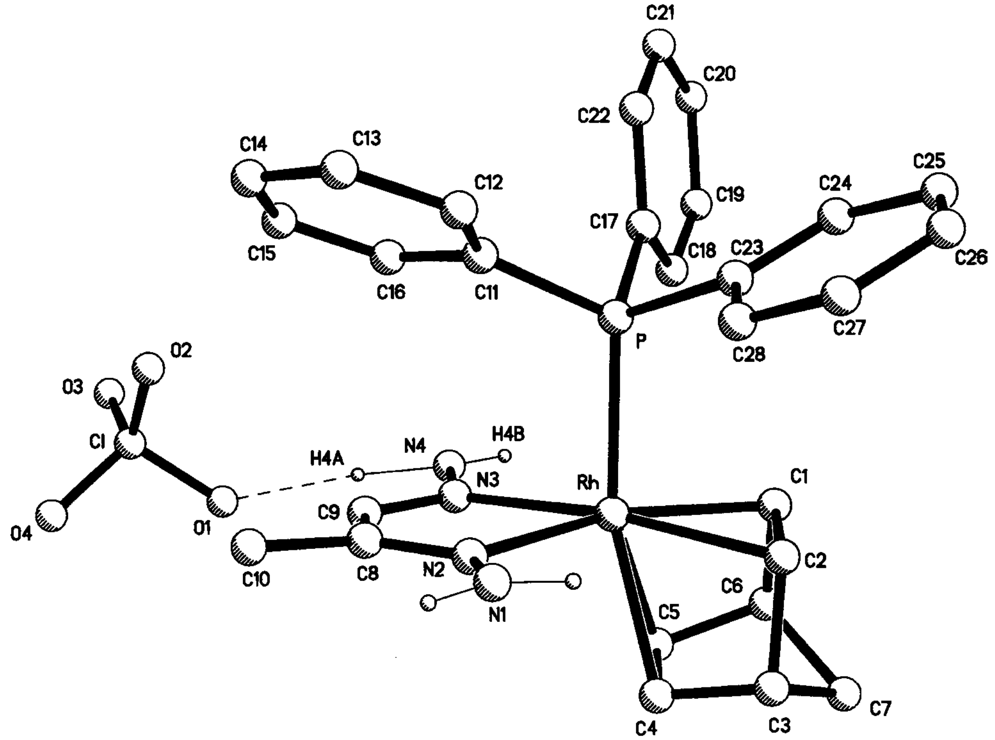

Fig. 2. PLUTO view of **2** showing the atomic numbering. The hydrogen atoms have been omitted for clarity.

with the perchlorate group forming chains along the $x$-axis.

As shown in Fig. 3, compound **4** also shows a distorted tbp geometry for the cation (Table 3) but now the diimine occupies axial–equatorial sites, so that the equatorial plane is occupied by one atom of the LL ligand N2, one of the olefinic bonds C1122 of the Nbd group and the P atom of the $PPh_3$ ligand. The other olefinic bond C4455 and the other N1 atom of the diimine are in axial positions. In this case, the rhodium atom is practically included in the P1N2C11122 plane. This plane forms an angle of 58.9(3)° with the plane containing the diolefinic carbon atoms of the Nbd ligand. The Rh–N1 axial distance, 2.053(8) Å, is slightly longer than that found in $[Rh(Cod)(DAP)]^+$, 2.027(8) Å, containing an axial pyridine ligand *trans* to an olefinic bond in a tbp geometry [24]. This Rh–N1 distance is shorter than the Rh–N2 equatorial distance, 2.225(8) Å, suggesting good σ-donor properties of the bda ligand. Shorter axial than equatorial Pt–N distances have also been observed in pentacoordinated compounds containing 2,9-$Me_2$-1,10-phenanthroline [19]. Also the Rh–P equatorial distance (2.398(3) Å) in complex **4** is longer than the Rh–P axial distance in compounds **1** and **2** (Table 3). The C8–C9 distance (1.48(1) Å) is similar to the one found in **1** due to the repulsion between the two methyl substituents in the diimine ligand. Furthermore, the planar phenyl $N$-substituents are twisted 26.8(3)° from each other and twisted 70.5(3) and 88.6(3)° respect to the RhN2C9C8N1 plane. These features may be due to the repulsive interaction between the two methyl groups and the two phenyl rings. Steric hindrance due to the

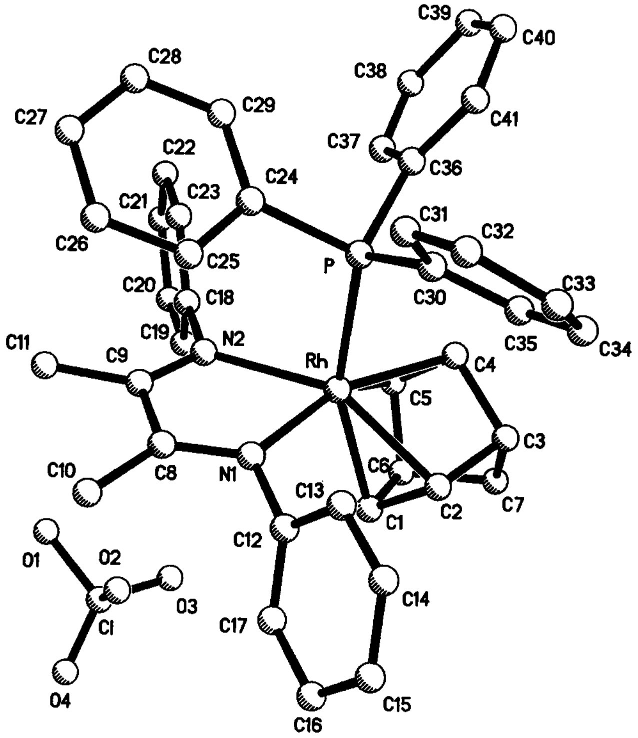

Fig. 3. PLUTO view of **4** showing the atomic numbering. The hydrogen atoms have been omitted for clarity.

Table 1
Crystal and refinement data for [Rh(Nbd)(Bdh)(PPh$_3$)]ClO$_4$ (**1**), [Rh(Nbd)(Pvdh)(PPh$_3$)]ClO$_4$ (**2**) and [Rh(Nbd)(Bda)(PPh$_3$)]ClO$_4$ (**4**)

| | **1** | **2** | **4** |
|---|---|---|---|
| Empirical formula | $C_{29}H_{33}ClN_4O_4PRh\cdot 1/2CH_2Cl_2$ | $C_{28}H_{31}ClN_4O_4PRh$ | $C_{41}H_{39}ClN_2O_4PRh$ |
| $M_r$ | 713.39 | 656.9 | 793.07 |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/c$ | $P2_1/n$ |
| $a$ (Å) | 11.0715(7) | 14.472(2) | 10.960(5) |
| $b$ (Å) | 14.0915(8) | 10.681(4) | 18.960(4) |
| $c$ (Å) | 11.6597(6) | 18.585(3) | 17.621(4) |
| $\alpha$ (°) | 79.920(6) | | |
| $\beta$ (°) | 71.398(5) | 103.56(1) | 103.13(3) |
| $\gamma$ (°) | 78.919(1) | | |
| $V$ (Å$^3$) | 1679.2(2) | 2792(1) | 3566(1) |
| $Z$ | 2 | 4 | 4 |
| $F(000)$ | 730 | 1344 | 1632 |
| $D_{calc.}$ (g cm$^{-3}$) | 1.411 | 1.56 | 1.477 |
| $\mu$ (mm$^{-1}$) | 6.341 | 8.06 | 6.44 |
| Scan technique | $\omega/2\theta$ | $\omega/2\theta$ | $\omega/2\theta$ |
| Data collected | (0, −16, −12) to (11,16,13) | (−17,0,0) to (16,12,22) | (−13,0,0) to (12,22,20) |
| $\theta$ range | 2.22–66.6 | 1.43–24.98 | 1.60–25.22 |
| Reflections collected | 5486 | 4769 | 6475 |
| Independent reflections | 5486 | 4618 ($R_{int} = 0.0665$) | 6263 ($R_{int} = 0.106$) |
| Observed reflections $(I) \geq 2\sigma(I)$ | 4950 | 2175 | 2939 |
| Data/parameters | 5486/352 | 4618/357 | 6263/427 |
| $R$ [a] | 0.077 | 0.051 | 0.077 |
| $R_{w_F}$ [b] | 0.22 | 0.13 | 0.19 |

[a] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$.

[b] $R_{w_F} = [\Sigma[w(F_o^2 - F_c^2)]^2/[\Sigma[w(F_o^2)^2]]^{1/2}$.

presence of these substituents in the diimine ligand, plus the phenyl groups of PPh$_3$ would favour the axial–equatorial coordination of bda; the triphenylphosphine ligand then occupies an equatorial site and the longer Rh–P distance alleviates steric repulsions. The occupation of axial–equatorial sites in complex **4** may be due to a combination of electronic and steric factors since the diimine in bda may be a better donor than the ones in complexes **1** and **2**.

NMR data of compounds **1** and **4** in CDCl$_3$ are collected in Table 4. According to $^{31}$P-NMR spectra, **1** and **4** undergo a phosphine dissociation equilibrium at (**4**) or above (**1**) room temperature and show well-resolved doublets due to rhodium-coordinated phosphine, in the range 273–213 K. Chemical shifts and $^1J$(Rh,P) coupling constants are as expected [11]. Their $^1$H-NMR spectra confirm the diimine ligands being bonded through the imino groups and both methyl groups appear as a single resonance. The olefinic protons and also the methinic protons of Nbd show only one resonance each in the range 273–213 K, indicating dynamic behaviour due to Berry pseudorotation [12] or to opening of the chelate ring [21]; the alkene chemical shifts, related to the geometry of norbornadiene pentacoordinated compounds in solution [10], suggest a trigonal bipyramidal geometry for these compounds also in solution. Compounds **2** and **3** are insoluble in CDCl$_3$.

In acetone solutions, measurements of the equivalent conductivities of complexes **2**–**4** at 273 K at different concentrations gave plots of the Onsager equation $\Lambda_e = \Lambda_o - A\sqrt{c_e}$ for which $A$ values agree with those calculated for 2:1 electrolytes [25], complex **1** shows intermediate $A$ values between those corresponding to 2:1 and 1:1 electrolytes, as shown in Table 5. This suggests that the formation of binuclear cationic complexes with bridging LL ligands in solution is less likely for Bdh compared with Pvdh and Gdh, in keeping with the lower tendency of biacetyl derivatives to behave as bridges [26]. Bda in compound **4** also behaves as a bridging ligand, likely due to the opening of the chelate that allows the ligand to adopt the *trans* conformation

Table 2
Hydrogen bond geometry (Å) and (°) for **1** and **2**

| N–H···O | $d$(N–H) | $d$(H···O) | $d$(N···O) | ∠NHO |
|---|---|---|---|---|
| **1** | | | | |
| N4–H4B···O1 | 1.00 | 2.65 | 3.04(2) | 103 |
| N1–H1A···O2 [a] | 0.86 | 2.54 | 3.28(2) | 146 |
| **2** | | | | |
| N4–H4A···O1 | 1.23 | 1.89 | 3.12(1) | 174.4 |
| N4–H4B···O3 [b] | 0.83 | 2.42 | 3.21(4) | 160.0 |

[a] $x+1, y, z$.

[b] $-x, -y+1, -z$.

Table 3
Selected bond lengths (Å) and angles (°) for **1**, **2** and **4**

| | 1 | 2 | 4 |
|---|---|---|---|
| *Bond lengths* | | | |
| Rh–C(1) | 2.102(9) | 2.08(1) | 2.10(1) |
| Rh–C(2) | 2.074(9) | 2.10(1) | 2.11(1) |
| Rh–C(4) | 2.208(9) | 2.16(1) | 2.20(1) |
| Rh–C(5) | 2.200(9) | 2.18(1) | 2.15(1) |
| Rh–N(1) | | | 2.053(8) |
| Rh–N(2) | 2.168(7) | 2.20(1) | 2.225(8) |
| Rh–N(3) | 2.224(4) | 2.19(1) | |
| Rh–P | 2.313(2) | 2.332(3) | 2.398(3) |
| Rh–C1122 | 1.97(1) | 1.95(1) | 1.98(1) |
| Rh–C4455 | 2.10(1) | 2.04(1) | 2.07(1) |
| C(1)–C(2) | 1.39(2) | 1.50(2) | 1.41(2) |
| C(4)–C(5) | 1.34(2) | 1.47(2) | 1.35(2) |
| C(8)–C(9) | 1.46(2) | 1.40(2) | 1.48(1) |
| *Bond angles* | | | |
| C1122–Rh–P | 96.7(3) | 94.8(4) | 137.5(4) |
| C4455–Rh–P | 161.6(4) | 162.2(5) | 101.9(4) |
| C1122–Rh–C4455 | 69.6(4) | 69.4(6) | 68.2(5) |
| N(1)–Rh–N(2) | | | 74.7(3) |
| N(2)–Rh–N(3) | 72.0(3) | 72.7(3) | |
| N(1)–Rh–C1122 | | | 93.7(4) |
| N(1)–Rh–C4455 | | | 160.8(4) |
| N(2)–Rh–C1122 | 155.7(4) | 135.5(4) | 128.3(5) |
| N(2)–Rh–C4455 | 97.3(3) | 103.1(5) | 110.9(4) |
| N(3)–Rh–C1122 | 130.2(4) | 150.2(4) | |
| N(3)–Rh–C4455 | 104.7(4) | 98.2(5) | |
| N(1)–Rh–P | | | 95.7(2) |
| N(2)–Rh–P | 90.8(2) | 93.8(2) | 94.2(2) |
| N(3)–Rh–P | 93.5(2) | 91.9(2) | |
| C(1)–Rh–C(2) | 38.7(4) | 42.2(6) | 39.2(5) |
| C(4)–Rh–C(5) | 35.3(4) | 39.5(6) | 36.0(4) |

and alleviates steric strains in the *cis* conformation. $^{31}$P-NMR data of compounds **1**–**4** in acetone-$d_6$ (Table 4) also show phosphine dissociation equilibrium at room temperature and well-resolved doublets in the range 273–213 K. Their $^1$H-NMR spectra show the expected resonances for the diimine bonded ligands and one resonance for the methinic protons of Nbd unmodified down to 213 K (Table 4). The olefinic protons of compounds **1**, **3** and **4** show only one broad singlet in the 273–213 K range, but in compound **2** (LL = Pvdh) they show at 303 K one resonance at 3.53 ppm that on lowering the temperature broadens and collapses to give two resonances at 273 K. The signal at higher field coincides with that of **1** (3.49 ppm) while the signal at lower field coincides with that of **3** (3.55 ppm). This feature may be due to the existence in solution of dimers, as shown by the conductivity data, with diimine bridging ligand, so that the H–C=N fragment is bonded to one of the rhodium atoms and the $CH_3$–C=N fragment to the other rhodium atom.

Previously we have reported on neutral pentacoordinated compounds containing Bdh [27]. We have now studied neutral pentacoordinated compounds containing Pvdh and Gdh. [Rh(Cl)(diolefin)(LL)] (LL = Pvdh, diolefin = Nbd, **5**, Cod, **6**; LL = Gdh, diolefin = Nbd, **7** Cod, **8**) can be easily obtained by reacting [Rh(diolefin)Cl]$_2$ with LL in dichloromethane. In their IR spectra the $\nu$(C=N) vibrations, slightly modified upon coordination, indicate bonding through both imino nitrogens and the weak $\nu$(Rh–Cl) confirm chlorine coordination to the rhodium atom. $\nu$(N–H) are displaced towards lower frequencies, as in analogous [Rh(Cl)(Cod)(Bdh)] [27], due to the intramolecular N–H···Cl–Rh hydrogen bond [28]. The ability of chlorine bonded to metal atoms to establish these interactions has recently been reviewed [29]. These compounds are only soluble in methanol where they undergo extended chloride dissociation (conductivity range for 1:1 electrolytes: 80–115 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ [30]). Their high insolubility precluded any NMR measurement.

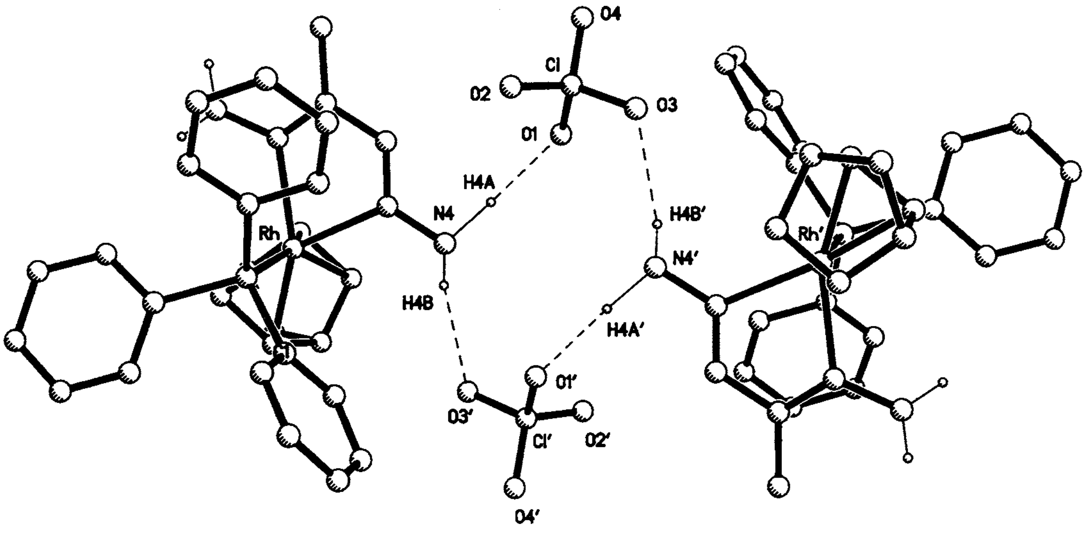

Fig. 4. PLUTO of the 'dimer units' showing the hydrogen bonds for **2**.

Table 4
Selected NMR data for the [Rh(Nbd)(LL)(PPh$_3$)]ClO$_4$ complexes

| Compound | Temperature (K) | LL | | | Nbd | | $^{31}$P-NMR |
|---|---|---|---|---|---|---|---|
| | | H–C=N | NH$_2$ | CH$_3$ | =CH | CH | |
| **1** (LL = Bdh) | 313 [a] | | 6.18 | 1.63 | 3.39 | 3.67 | 34.37(s, br) |
| | 293 [a] | | 6.22 | 1.58 | 3.32 | 3.64 | 34.74(d, $J = 139$) |
| | 293 [b] | | 6.82 | 1.72 | 3.47 | 3.62 | 31.68(s, br) |
| | 273 [b] | | 6.93 | 1.73 | 3.49 | 3.65 | 32.24(d, $J = 134$) |
| **2** [b] (LL = Pvdh) | 303 | 7.10 | 7.34; 6.67 | 1.68 | 3.53 | 3.59 | 29.75(s, br) |
| | 283 | 7.09 | 7.43; 6.75 | 1.68 | 3.52(br) | 3.59 | 29.80(d, $J = 132$) |
| | 273 | 7.08 | 7.47; 6.77 | 1.67 | 3.49; 3.55 | 3.57 | 29.72(d, $J = 134$) |
| **3** [b] (LL = Gdh) | 303 | 7.12 | 7.30 | | 3.56 | 3.56 | 27.57(s, br) |
| | 273 | 7.11 | 7.41 | | 3.55 | 3.55 | 27.11(d, $J = 132$) |
| **4** (LL = Bda) | 293 [a] | | | 2.10 | 3.06 | 3.37 | 21.55(s, br) |
| | 273 [a] | | | 2.09 | 3.04 | 3.39 | 22.18(d, $J = 129$) |
| | 293 [b] | | | 2.18 | 3.07 | 3.48 | 22.50(s, br) |
| | 273 [b] | | | 2.17 | 3.04 | 3.50 | 23.33 (d, $J = 130$) |

[a] CDCl$_3$.
[b] Acetone-$d_6$.

When the above reaction is performed in the presence of SnCl$_2$, pentacoordinated trichlorostannate compounds [Rh(SnCl$_3$)(diolefin)(LL)] (LL = Pvdh, diolefin = Nbd, **9**, Cod, **10**; LL = Gdh, diolefin = Nbd, **11** Cod, **12**) are obtained that show covalently bonded SnCl$_3$ groups [31] along with diimino bonded ligands. In acetone solution norbornadiene complexes behave almost as non-electrolytes while 1,5-cyclooctadiene compounds undergo extended ionic dissociation. In methanol solution compounds **9**–**12** behave as 1:1 electrolytes. Reported [Rh(Cod)(Bdh)](SnCl$_3$) is ionic [27]. $^{119}$Sn-NMR spectra of Pvdh compounds **9** and **10** in acetone solution show a broad singlet at ca. 170 ppm that indicates tin dissociation at room temperature, most likely via SnCl$_3^-$ dissociation on account of the conductivity data. Only for compound **9** has it been possible to observe at 183 K a doublet due to SnCl$_3$ coordinated to rhodium and the values of chemical shift and coupling constant are in agreement with analogous compounds containing other diimines [21,27]. Accordingly with this, in its $^1$H-NMR spectrum the olefinic and methinic resonances are broad singlets at room temperature, coalesce and resolve into two signals each at 183 K. The low-temperature spectrum agrees with a square pyramidal limiting structure with the SnCl$_3^-$ group occupying the axial position similar to that found in related [Rh(SnCl$_3$)(Nbd)(glyoxalbis(cyclohexylimine))] [21]; the chemical shift of the olefinic resonances of norbornadiene in the lower field range also indicates this structure [10]. The $^1$H-NMR spectrum of **10** shows at room temperature two resonances for the olefinic protons of cyclooctadiene, most likely due to two different species in solution, i.e. [Rh(SnCl$_3$)(Cod)(Pvdh)] and [Rh(Cod)(Pvdh)]$^+$. Gdh complexes **11** and **12** are only soluble in CD$_3$OD and show the expected resonances for tetracoordinated compounds.

## 3. Experimental

The preparation of the metal complexes was carried out at room temperature (r.t.) under nitrogen by standard Schlenk techniques. [{M(L$_2$)Cl}$_2$] [32] were prepared as previously reported. α-Diimines [18,33] were synthesised according to known procedures.

Microanalysis were carried out with a Perkin–Elmer 240C microanalyser. Conductivities were measured in acetone or methanol solution with a Metrohm E 518 conductimeter. IR spectra were recorded with a Nicolet FTIR 740 spectrophotometer in the range 4000–50 cm$^{-1}$ using KBr pellets or nujol mulls between polyethylene sheets. NMR spectra were recorded with an XL-300 Varian spectrometer, $^1$H (TMS internal standard) and $^{31}$P (H$_3$PO$_4$ external standard) spectra were measured from CDCl$_3$, acetone-$d_6$ or CD$_3$OD solutions, $^{119}$Sn (SnMe$_4$ external standard) spectra were measured from 1:1 acetone–acetone-$d_6$ solutions. Mass spectra were recorded on a VG Autospec, by liquid secondary ion (LSI) MS using nitrobenzylalcohol as matrix and a caesium gun (Universidad de Zaragoza).

Table 5
Conductivity data for [Rh(Nbd)(LL)(PPh$_3$)]ClO$_4$ complexes

| Complex | $\Lambda_o$ [a] ($\Omega^{-1}$ cm$^2$ eq$^{-1}$) | $\Lambda_{exp}$ [a] | $\Lambda_{theor}$ [b] (1:1) | $\Lambda_{theor}$ [b] (2:1) |
|---|---|---|---|---|
| **1** (LL = Bdh) | 176 | 942 | 687 | 1335 |
| **2** (LL = Pvdh) | 174 | 1284 | 691 | 1340 |
| **3** (LL = Gdh) | 190 | 1378 | 713 | 1408 |
| **4** (LL = Bda) | 170 | 1427 | 676 | 1447 |

[a] Measured in acetone solution. From the Onsager's equation $\Lambda_e = \Lambda_o - A\sqrt{c_e}$ plot.
[b] Calculated according to Ref. [25].

### *3.1. Preparation of complexes [Rh(Nbd)(LL)(PPh$_3$)]ClO$_4$*

To a $CH_2Cl_2$ solution of [{Rh($L_2$)Cl}$_2$] (0.06 mmol) and triphenylphosphine (0.12 mmol) was added an acetone solution of the stoichiometric amount (0.12 mmol) of $AgClO_4$. After 30 min the formed AgCl was filtered. The obtained solution was evaporated to dryness and the residue solved in dichloromethane. Addition of the required amount (0.12 mmol) of the corresponding ligand to this solution followed by addition of diethyl ether gave precipitates that were filtered off, washed with diethyl ether and vacuum dried. Yields: 60–80%.

#### *3.1.1. [Rh(Nbd)(Bdh)(PPh$_3$)]ClO$_4$ (**1**)*

IR (KBr, $cm^{-1}$): 3404(m), 3392(m), 3304(m), $\nu$(N–H); 1607(m), $\nu$(C=N); 1098(vs), $\nu$(Cl–O). FAB MS: Calc. for $C_{29}H_{33}N_4P^{103}Rh$: 571; observed: 571 [$M^+$]. Anal. Calc. for $C_{29}H_{33}ClN_4O_4PRh\cdot0.5CH_2Cl_2$: C, 49.67; H, 4.80; N, 7.85; Found: C, 49.19 H, 4.99; N, 7.54%.

#### *3.1.2. [Rh(Nbd)(Pvdh)(PPh$_3$)]ClO$_4$ (**2**)*

IR (KBr, $cm^{-1}$): 3422(m), 3389(m), 3297(m), 3207(w), $\nu$(N–H); 1585(m), $\nu$(C=N); 1111(s), 1094(s), $\nu$(Cl–O). FAB MS: Calc. for $C_{28}H_{31}N_4P^{103}Rh$: 557; observed: 557 [$M^+$]. Anal. Calc. for $C_{28}H_{31}ClN_4O_4PRh$: C, 51.20; H, 4.76; N, 8.53; Found: C, 50.80 H, 4.71; N, 8.39%.

#### *3.1.3. [Rh(Nbd)(Gdh)(PPh$_3$)]ClO$_4$ (**3**)*

IR (KBr, $cm^{-1}$): 3422(s), 3387(m), 3295(s), 3218(m), 3204(m) $\nu$(N–H); 1591(m), $\nu$(C=N); 1112(s), 1090(s), $\nu$(Cl–O). FAB MS: Calc. for $C_{27}H_{29}N_4P^{103}Rh$: 543; observed: 543 [$M^+$]. Anal. Calc. for $C_{27}H_{29}ClN_4O_4PRh\cdot0.5CH_2Cl_2$: C, 49.28; H, 4.48; N, 8.44; Found: C, 49.25 H, 4.52; N, 8.25%.

#### *3.1.4. [Rh(Nbd)(Bda)(PPh$_3$)]ClO$_4$ (**4**)*

IR (KBr, $cm^{-1}$): 1590(m), $\nu$(C=N); 1090(vs), $\nu$(Cl–O). FAB MS: Calc. for $C_{41}H_{39}N_2P^{103}Rh$: 693; observed: 693 [$M^+$]. Anal. Calc. for $C_{41}H_{39}ClN_2O_4PRh$: C, 62.09; H, 4.96; N, 3.53; Found: C, 61.66 H, 4.71; N, 3.42%.

#### *3.1.5. Preparation of complexes [RhCl(diolefin)(LL)]*

To a $CH_2Cl_2$ solution of [{Rh($L_2$)Cl}$_2$] (0.06 mmol) was added two equivalents (0.12 mmol) of the corresponding ligand upon which precipitation of red complexes occurred that were filtered off, washed with dichloromethane and vacuum dried. Yields: 60–80%.

#### *3.1.6. [RhCl(Nbd)(Pvdh)] (**5**)*

IR ($cm^{-1}$): 3318(m), 3266(m), 3131(s), 3087(s) $\nu$(N–H); 1589(m) $\nu$(C=N); 280(w) $\nu$(Rh–Cl). $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$): 40 (MeOH). Anal. Calc. for $C_{10}H_{16}ClN_4Rh$: C, 36.33; H, 4.88; N, 16.95; Found: C, 36.17; H, 4.78; N, 16.70%.

#### *3.1.7. [RhCl(Cod)(Pvdh)] (**6**)*

IR ($cm^{-1}$): 3315(m), 3256(m), 3174(s), 3088(s) $\nu$(N–H); 1588(m) $\nu$(C=N); 278(w) $\nu$(Rh–Cl). $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$): 53 (MeOH). Anal. Calc. for $C_{11}H_{20}ClN_4Rh$: C, 38.11; H, 5.82; N, 16.16; Found: C, 37.96; H, 5.76; N, 15.61%.

#### *3.1.8. [RhCl(Nbd)(Gdh)] (**7**)*

IR ($cm^{-1}$): 3302(s), 3281(s), 3112(s), 3091(s) $\nu$(N–H); 1578(s) $\nu$(C=N); 288(w) $\nu$(Rh–Cl). $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$): 59 (MeOH). Anal. Calc. for $C_9H_{14}ClN_4Rh$: C, 34.14; H, 4.46; N, 17.70; Found: C, 34.08; H, 3.86; N, 17.64%.

#### *3.1.9. [RhCl(Cod)(Gdh)] (**8**)*

IR ($cm^{-1}$): 3323(m), 3274(m), 3140(s), 3091(s) $\nu$(N–H); 1573(s) $\nu$(C=N); 278(w) $\nu$(Rh–Cl). $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$): 57 (MeOH). Anal. Calc. for $C_{10}H_{18}ClN_4Rh$: C, 36.11; H, 5.45; N, 16.84; Found: C, 35.67; H, 5.14; N, 16.47%.

### *3.2. Preparation of trichlorostannato complexes*

To a $CH_2Cl_2$ solution of [{Rh($L_2$)Cl}$_2$] (0.06 mmol) was added two equivalents (0.12 mmol) of the corresponding ligand. Addition of a methanol solution of $SnCl_2$ (0.12 mmol) led to red solutions. Removal of $CH_2Cl_2$ gave red solids that were filtered off, washed with MeOH and vacuum dried. Yields: 60–90%.

#### *3.2.1. [Rh(SnCl$_3$)(Nbd)(Pvdh)] (**9**)*

IR ($cm^{-1}$): 3354(m), 3274(m), 3223(m), 3203(m) $\nu$(N–H); 1584(m) $\nu$(C=N); 298(m), 258(m) $\nu$(Sn–Cl). $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$): 15 (acetone), 90 (MeOH). $^1$H-NMR (acetone-$d_6$, 183 K): $\delta$ 7.51 (s, H–C=N), 7.37 (s, $NH_2$), 6.73 (s, $NH_2$), 2.08 (s, $CH_3$), 4.07 (2H, =CH and 1H, CH), 3.67 (2H, =CH), 3.24 (1H, CH). $^1$H-NMR (acetone-$d_6$, 293 K): $\delta$ 6.80 (s, $NH_2$), 6.14 (s, $NH_2$), 3.81 (4H, =CH), 3.65 (2H, CH), the other resonances are the same as those at 193 K. $^{119}$Sn-NMR (acetone-$d_6$, 183 K): $\delta$ 178 (d; $^1$J(Rh,Sn), 543Hz). $^{119}$Sn-NMR (acetone-$d_6$, 293 K): $\delta$ 177 (br). Anal. Calc. for $C_{10}H_{16}Cl_3N_4RhSn$: C, 23.09; H, 3.10; N, 10.77; Found: C, 22.80; H, 3.03; N, 10.51%.

#### *3.2.2. [Rh(SnCl$_3$)(Cod)(Pvdh)] (**10**)*

IR ($cm^{-1}$): 3352(m), 3279(m), 3268(m), 3221(m), 3191(m) $\nu$(N–H); 1584(m) $\nu$(C=N); 291(m), 265(m), 245(m) $\nu$(Sn–Cl). $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$): 67 (acetone), 75 (MeOH). $^1$H-NMR (acetone-$d_6$): $\delta$ 7.54 (s, H–C=N), 6.85 (br, $NH_2$), 6.65 (br, $NH_2$), 6.16 (br, $NH_2$), 2.12 (s, $CH_3$), 4.45 (br, =CH), 4.27 (br, =CH). $^{119}$Sn-NMR (acetone-$d_6$): $\delta$ 160 (br). Anal. Calc. for $C_{11}H_{20}Cl_3N_4RhSn$: C, 24.64; H, 3.76; N, 10.45; Found: C, 24.88 H, 3.74; N, 10.21%.

### 3.2.3. *[Rh(SnCl$_3$)(Nbd)(Gdh)]* (***11***)

IR (cm$^{-1}$): 3345(s), 3274(m), 3204(m) $\nu$(N–H); 1571(m) $\nu$(C=N); 339(m), 308(m) $\nu$(Sn–Cl). $\Lambda_M$ ($\Omega^{-1}$ cm$^2$ mol$^{-1}$): 18 (acetone), 90 (MeOH). $^1$H-NMR ($CD_3OD$): $\delta$ 7.12 (s, H–C=N), 4.40 (br, =CH), 3.97 (br, CH). Anal. Calc. for $C_9H_{14}Cl_3N_4RhSn$: C, 21.36; H, 2.79; N, 11.07; Found: C, 21.78; H, 2.76; N, 10.93%.

### 3.2.4. *[Rh(SnCl$_3$)(Cod)(Gdh)]* (***12***)

IR (cm$^{-1}$): 3373(s), 3267(s), 3197(m) $\nu$(N–H); 1565(m) $\nu$(C=N); 293(m), 263(m) $\nu$(Sn–Cl). $\Lambda_M$ ($\Omega^{-1}$ cm$^2$ mol$^{-1}$): 46 (acetone), 102 (MeOH). $^1$H-NMR ($CD_3OD$): $\delta$ 7.17 (s, H–C=N), 4.75 (br, =CH). Anal. Calc. for $C_{10}H_{18}Cl_3N_4RhSn$; C, 23.00; H, 3.47; N, 10.73; Found: C, 23.24 H, 3.41; N, 10.74%.

### 3.3. *Crystallography*

Prismatic single crystals of **1**, **2** (yellow) and **4** (red) were grown by layering dichloromethane solutions with diethyl ether. The data for **1** were collected up to $2\theta = 134°$ with graphite-monochromated Cu–K$_\alpha$ radiation ($\lambda = 1.5418$ Å) on a Seifert XRD 3000s non-conventional four-cycle diffractometer using an $\omega/2\theta$ scan mode. For **2** and **4** the data were collected on an Enraf–Nonius CAD4 diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) and unit cell constants refined by least-squares fitting of the $\theta$ values of 25 reflections, with $2\theta$ range of 5–24° for **2** and 13–27° for **4**. Three check reflections were monitored after every 97 reflections for the three compounds. No appreciable drop in the intensities of standard reflections was observed for **1** and **2**, while for **4** a decay of 10% was observed.

In each case the heavy atoms have been located by the Patterson method and the rest of the atoms by Fourier syntheses. The refinement was done by full-matrix least-squares on $F^2$ (SHELXL97) [34] with the following differences: for **1** and **4** some non-resolvable disorder from thermal motion has been found for the oxygen atoms of the perchlorate group, and because of this, these atoms were refined only isotropically. In addition, for **1** solvent was found in the last cycles of refinement with a very important non-resolvable positional disorder, which was included and their positions fixed. The best $R$ factor was obtained with $1/2CH_2Cl_2$. The rest of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and refined as riding on a carbon-bonded atom with common isotropic displacement parameters, except for the hydrogen atoms of the amino groups, which were found as the first peaks in a Fourier difference syntheses, including fixed positions. The largest residual peak for **1** in the final Fourier difference map was 2.3 e Å$^{-3}$ near the disordered solvent molecule and for **2** and **4**, 0.9 and 1.9 e Å$^{-3}$, respectively, in the vicinity of the Rh atom.

## 4. Conclusions

Pentacoordinated [Rh(Nbd)(LL)(PPh$_3$)]ClO$_4$ (LL = α-diimine) adopts distorted trigonal bipyramid geometry. Dihydrazones prefer the occupancy of equatorial positions and a combination of electronic and steric factors makes biacetyldianyl occupy axial–equatorial sites. Dihydrazone compounds show intermolecular hydrogen bond N-H$\cdots$OClO$_3$ linkages, weaker in the biacetyl derivative. In acetone solution Gdh, Pvdh and Bda behave as bridging ligands. In solution [Rh(SnCl$_3$)(Nbd)(Pvdh)] prefers a square pyramidal structure with SnCl$_3$ in apical position at 183 K.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 136303 for compound **1**, no. 136304 for compound **2** and no. 136305 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ [Fax +44(1223)336-033] or e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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