# Dirhodium(II) Complexes with Bi- and Tri-dentate Nitrogen-containing Ligands

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The dirhodium(II) formamidinate complex $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ reacted with 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen), molar ratio 1:1, giving $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(L\text{–}L)]$ (L–L = bipy **1** or phen **4**). Both complexes in acetonitrile solution behave as 1:2 electrolytes showing that both trifluoroacetate groups are weakly bonded, so that the species in MeCN is very likely $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(L\text{–}L)L_n][CF_3CO_2]_2$ (L = MeCN, *n* = 2 or 3). Proton NMR spectra show unambiguously that **1** and **4** exist in acetonitrile solution as a mixture (1:1) of two isomers, **1a** and **4a**, possessing an axial–equatorial chelated L–L group, and **1b** and **4b** with the chelating L–L in the equatorial plane. Isomers **a** and **b** interconvert on treating **1** and **4** with pyridine or cyclohexyl isocyanide (**a** ⟶ **b**) or by thermal reaction (**b** ⟶ **a**). When the reaction with L–L was carried out in the ratio 1:2 the complexes $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}(\sigma\text{-}O_2CCF_3)_2(L\text{–}L)_2]$ (L–L = bipy **2** or phen **5**) were obtained. In these complexes, which undergo dissociation of both trifluoroacetate groups in MeCN, the ligands are face-to-face co-ordinated in equatorial position. The parent complex reacted also with the new trinucleating compound 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine (dpnapy) leading to the monoadduct $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(dpnapy)]$. Two isomers were obtained depending on the experimental conditions. As determined by $^1H$ and $^{31}P$ NMR spectroscopy, mild conditions lead to an isomer containing the phosphorus atom in axial position and the naphthyridine fragment bridging the dirhodium core. Under more vigorous conditions the P-equatorial isomer with the bidentate L–L fragment axially–equatorially chelated was obtained.

The chemistry of dirhodium(II) complexes has been the subject of intensive studies because they are involved in many important catalytic and biochemical processes.[1] Dirhodium(II) carboxylates are in fact the most effective for intermolecular reactions involving diazo carbonyl compounds, *via* carbene addition to multiple bonds,[2] as well as giving rise to a significant increase in survival time of mice bearing Ehrlich ascites or Leukaemia 1210. Unfortunately the antitumoral activity of these complexes parallels their toxicity.[3]

Recently the chemistry of the dirhodium(II) complexes has received an impressive development arising from the introduction into the 'lantern' structure of anionic, N-donor bidentate ligands.[4] The presence of these ligands on the one hand results in a dramatic effect on the redox properties of the related complexes, facilitating the formation of mixed-valent dirhodium(II,III) derivatives, on the other hand it causes an improvement in their catalytic and biochemical activity. The complex $[Rh_2(HNCOMe)_4]$ achieves, in intermolecular alkene cyclopropanation reactions, a *trans*(*anti*) stereoselectivity higher than that of the corresponding tetracarboxylate derivatives[5] while the complexes $[Rh_2(5S\text{-}L)_4]$ and $[Rh_2(5R\text{-}L)_4]$ (HL = methyl 2-pyrrolidone-5-carboxylate) promote high enantioselectivity in the intramolecular cyclopropanation of allyl diazoacetates.[6] Concerning the biochemical activity, the mixed-ligand complex $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$[7a] exhibits against the Ehrlich ascites an antitumoral activity comparable with that of the well known *cis*-$[Pt(NH_3)_2Cl_2]$ and has a remarkable low toxicity.[7b] Furthermore the complex $[Rh_2(O_2CMe)_2(L\text{–}L)_2(H_2O)_2][MeCO_2]_2$ [L–L = 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy)] shows against KB cells *in vitro* a cytostatic activity comparable with that of $[Rh_2(O_2CMe)_4]$.[7c]

So the introduction into the lantern structure of ligands other than carboxylate allows a greater variation in the molecular patterns and hence the chemical reactivity of dirhodium(II) complexes.

As a part of a project aimed at synthesising new $Rh_2^{4+}$ complexes, we report in this paper the synthesis and spectroscopic characterization of a series of dirhodium(II) complexes obtained by treating $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ with aromatic nitrogen-donor ligands, *e.g.* 2,2′- or 4,4′-bipy, phen, pyrazine and 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine (dpnapy). This complex has proven to be an ideal starting material for the synthesis of other dirhodium(II) complexes. Its chemistry is characterized, in addition to the usual axial reactivity, also by a remarkable lability of the trifluoroacetate groups, which leads to mild conditions for the co-ordination of neutral mono- and bidentate ligands at the equatorial positions without rupture of the $Rh\{CH(NC_6H_4Me\text{-}p)_2\}_2Rh$ fragment.

## Results and Discussion

*Reactions of* $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ *with 2,2′-Bipyridine.*—Treatment of the complex $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ with an equimolar quantity of 2,2′-bipyridine in diethyl ether yields, after minimum work-up, $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(2,2'\text{-bipy})]$ **1**. Under more vigorous reaction conditions $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(\sigma\text{-}O_2CCF_3)_2(2,2'\text{-bipy})_2]$ **2** is formed. Both new complexes are air-stable crystalline solids for which satisfactory analytical data have been obtained. Their structures follow from their spectroscopic properties and conductivity measurements. The solid-state IR spectrum of **1** shows, in addition to bands associated with the formamidinate fragment, a medium-intensity absorption at 1642 and a strong one at 1673 cm$^{-1}$. The lower value is consistent with those of chelating or bridging fluorocarboxylate groups while the higher suggests the presence of a monodentate $CF_3CO_2$ group. Conductivity measurements show that, independently of the solid-state co-ordination mode of the two trifluoroacetate groups, both are weakly bonded and in co-ordinating solvents are easily displaced. Complex **1**, which is soluble only in polar organic solvents, is non-conducting in dichloromethane while the value of 250 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ found in MeCN indicates it to behave as a 1 : 2 electrolyte with extensive dissociation of the two trifluoroacetate groups. In addition solution IR spectra, recorded in $CH_2Cl_2$ and MeCN, show single absorptions at 1673 and 1695 cm$^{-1}$, respectively. The conductivity and IR data suggest that the species in acetonitrile solution is $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(2,2'\text{-bipy})L_n][CF_3CO_2]_2$ (L = MeCN) while in dichloromethane the solid-state structure is very likely retained.

Inspection of the pyridyl proton resonances of complex **1** clearly shows (Fig. 1) the presence of two isomers in equal amounts. The $^1$H NMR spectrum displays twelve sets of resonances due to the pyridine rings rather than the expected four. Most signals show multiplet splitting due to three-bond coupling to neighbouring protons on the same ring. Among them two sets of four protons, with the right integral ratio, appear related to a species showing magnetically non-equivalent environments for the pyridyl rings (isomer **1a**) while the remaining four sets are related to a species **1b** with a diequatorial chelated bipy group. In particular the spectrum in $CD_3CN$ (the spectra in $CDCl_3$ are complicated by a series of resonances very likely arising from more than two isomers) at room temperature accounts for the two isomers, showing for the most deshielded H$^6$ protons three doublets centred at δ 9.05, 8.96 and 8.86 with intensity ratio 2 : 1 : 1. Also the other H$^3$, H$^4$ and H$^5$ protons give rise to three signals, with intensity ratio 2 : 1 : 1, and deshielded with respect to free bipy indicating a decrease in electron density on the co-ordinated ligand. The expected three signals due to the methine protons occur in an overlapping group in the range δ 7.75–7.9.

It is worth mentioning that $[Rh_2(O_2CMe)_4]$ reacts with bipy, independently of the molar ratio or experimental conditions, giving, as the only product, a species containing the bipy ligand chelated at the equatorial and axial positions.[8] The formation of isomer **1b** may be explained taking into account that the presence of the labile trifluoroacetate groups in the starting material easily allow axial–equatorial ⟶ diequatorial isomerization. This process for the parent complex is well established and has been fully investigated by using monodentate phosphines[9] or 2-(diphenylphosphino)pyridine.[10] The same process has been detected during a $^1$H NMR investigation of the reaction of $[Rh_2(O_2CMe)_2(MeCN)_4]^{2+}$ with the chelating ligands bipy and phen,[11] suggesting that the presence of equatorially co-ordinated labile ligands is required for equatorial reactivity in dirhodium(II) complexes. Furthermore while this work was in progress axial–equatorial ⟶ diequatorial isomerization, induced by MeOH, was reported for the complex $[Rh_2(O_2CMe)_4(bipy)]$ while a diequatorially co-ordinated bipy has been found in $[Rh_2(O_2CCF_3)_4(bipy)(thf)(H_2O)]$ (thf = tetrahydrofuran).[8]

*Interconversion* **1a** $\rightleftharpoons$ **1b**.—Isomer **1a** is converted into **1b** by treating complex **1** with pyridine (py) or cyclohexyl isocyanide. These experiments were performed in an NMR tube by adding by syringe an acetonitrile solution of py or $C_6H_{11}NC$ to a solution of **1** dissolved in the same solvent. In each case the $^1$H NMR spectra reveal the disappearance of the starting absorptions and the quantitative formation of species which show the two bipy halves in a magnetically equivalent environment. In the δ 7–10 region there are only four sets of signals attributable to bipy proton resonances, with the right integral ratio.

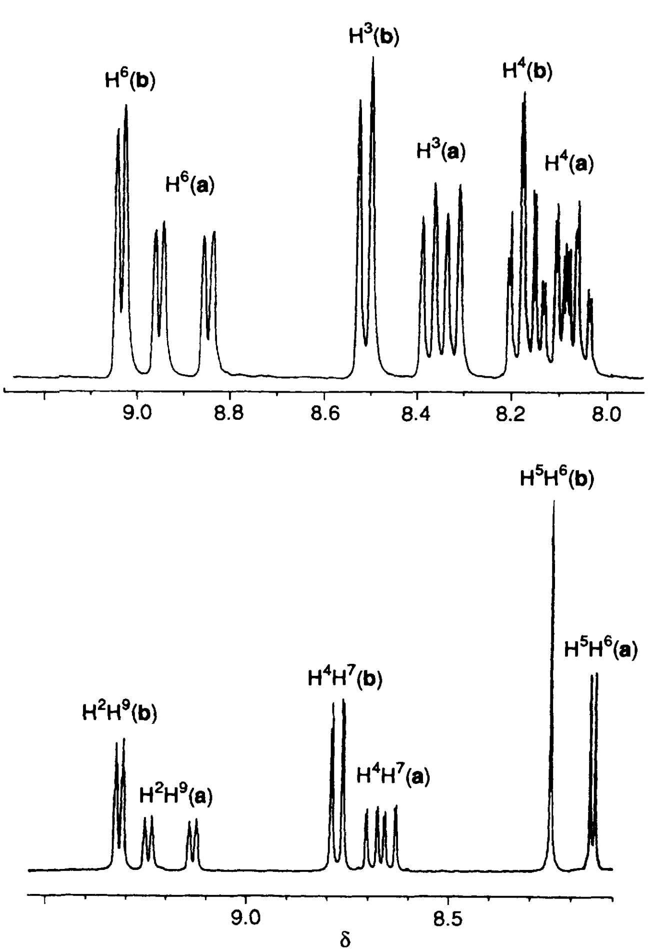
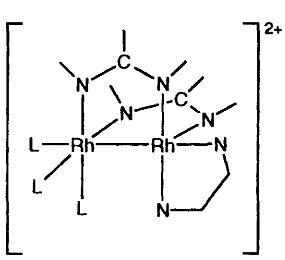
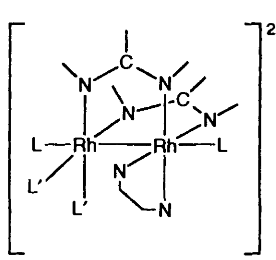


**Fig. 1** Section of the proton NMR spectra (300.13 MHz, $CD_3CN$) of complexes **1** (above) and **4** (below)



**1a** N—N = 2,2′-bipy, L = MeCN
**4a** N—N = phen, L = MeCN

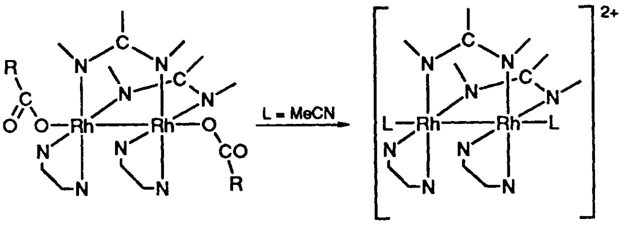


**1b** N—N = 2,2′-bipy, L = L′ = MeCN
**4b** N—N = phen, L = L′ = MeCN
**3** N—N = 2,2′-bipy, L = MeCN, L′ = $C_6H_{11}NC$

The isocyanide derivative has been also isolated by treating a dichloromethane solution of complex **1** with $C_6H_{11}NC$ in molar ratio 1:2. The complex $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(2,2'\text{-bipy})(C_6H_{11}NC)_2]$ **3**, which is a 1 : 1 and 1 : 2 electrolyte in $CH_2Cl_2$ and MeCN respectively, exhibits in the solid-state IR spectrum, in addition to the ν(CN) absorption at 2170 cm$^{-1}$, a single absorption at 1687 cm$^{-1}$ indicating that in the solid state both $CF_3CO_2$ groups are very likely monoco-ordinated at the axial positions. Moreover the $^1$H NMR spectrum, showing four sets of signals, reveals magnetic equivalence of the two pyridine rings. A well formed triplet centred at δ 8.01, arising from equivalent methine protons, is also present.

Isomer **1b** can be partly isomerized (75%) to **1a** in a thermal reaction (80 °C, 6 h) indicating that the latter is thermodynamically favoured. Further refluxing causes the appearance in the $^1$H NMR spectrum of several peaks due to complex decomposition.

Differently from the acetate derivative, the complex $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ reacts with an excess of bipy giving $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(\sigma\text{-}O_2CCF_3)_2\text{-}$

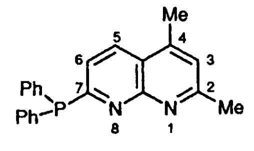


**2** N—N = 2,2′-bipy
**5** N—N = phen

(2,2′-bipy)$_2$] **2** containing both the bipy ligands in equatorial position. Dirhodium(II) complexes containing two equatorial α-diimine ligands are not unknown but their synthesis has been achieved by using mineral acids in order to displace the bridging ligands from the equatorial positions.[12] Complex **2**, which is a 1 : 1 and 1 : 2 electrolyte in $CH_2Cl_2$ and MeCN respectively, exhibits in the $^1H$ NMR spectrum only four sets of signals attributable to pyridine rings indicating that both ligands are symmetrically bonded to the dirhodium core. For example the $H^6$ protons give rise to a single set of signals at δ 8.34, namely at high field compared to the signals of the free bipy and complex **1**. The upfield shift of the α,α′-diimine protons may be due to increased shielding of the protons caused by π-back donation from dp orbitals of the metal to π* antibonding orbitals of the α-diimine, or ring-current effects of the cofacial pyridine. The last explanation seems more likely either because the double positive charge disfavours π donation or complexes **1** and **3**, which contain only one bipy group, show the opposite trend. The symmetrical arrangement of the ligands around the $Rh_2^{4+}$ core is also supported by the methine and methyl proton resonances which appear as singlets at δ 8.18 and 2.22, respectively. On the basis of the spectroscopic data we suggest that in complex **2** the two nitrogen ligands are co-ordinated face to face in equatorial position, analogously to what is found for $[Rh_2(O_2CMe)_2(phen)_2Cl_2]$.[12a]

*Reactions of* $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ *with* 1,10-*Phenanthroline*.—The reactions of $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ with 1,10-phenanthroline, molar ratio 1 : 1 or 1 : 2, occur readily yielding two compounds of empirical formula $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(phen)]$ **4** and $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(\sigma\text{-}O_2CCF_3)_2(phen)_2]$ **5**, respectively. The general similarity of the IR and $^1H$ NMR spectra and conductivity data of complexes **1** and **2** with those of **4** and **5**, respectively, implies that **1** and **4** and **2** and **5** are structurally similar. The $^1H$ NMR spectrum of **4**, in $CD_3CN$, once more shows the presence of isomers **a** and **b** in ratio 1.3 : 1. Treatment of **4** with $C_6H_{11}NC$ results in the formation of a new species analogous to **3** as confirmed by $^1H$ NMR spectroscopy, which shows the disappearance of isomer **a** and the formation of a single species having the two halves of phen in almost identical environments.

Structural assignment of complex **5** follows from the IR spectrum which shows a single $\nu_{asym}(CO_2)$ at 1688 cm$^{-1}$, and conductivity measurements which reveal complete dissociation of both trifluoroacetate groups. The $^1H$ NMR spectrum is very informative. It shows only one signal attributable to the methyl protons at δ 2.27 while the methine protons appear as a triplet centred at δ 8.34 confirming that the formamidinate groups are chemically as well as magnetically equivalent. In the pyridine region there are four sets of signals which, analogously to what is found for the bipy derivative, lie upfield with respect to those of free phen. The $H^2$ and $H^9$ protons appear as a doublet of doublets, centred at δ 8.54 ($^1J$ = 5.2, $^2J$ = 1.0 Hz). The signal at δ 8.15 is assigned to the $H^4$ and $H^7$ protons ($J$ = 8.1 Hz), while $H^5$ and $H^6$ appear as a singlet at δ 7.64. Finally the more deshielded protons $H^3$ and $H^8$ occur as a doublet of doublets centred at δ 7.48.



dpnapy

*Reactions of* $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ *with* 7-*Diphenylphosphino*-2,4-*dimethyl*-1,8-*naphthyridine*.—Two isomers were also obtained by treating the complex $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ with 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine, recently isolated by us.[13] This compound, which can be regarded as a combination of the short-bite 1,8-naphthyridine and 2-(diphenylphosphine)pyridine, reacts with 1 molar equivalent of the complex in diethyl ether solution at room temperature to give a green microcrystalline precipitate in high yield. This, according to the elemental analysis, corresponds to the monoadduct $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(dpnapy)]$ **6a**. It is an air-stable solid which dissolves easily in most common solvents, and behaves as a 1 : 1 electrolyte in acetonitrile and dichloromethane. The solid-state IR spectrum displays two strong absorptions at 1689 and 1636 cm$^{-1}$ pointing to the presence of non-equivalent trifluoroacetate groups. Attempts to obtain a single crystal suitable for an X-ray diffraction study failed. Useful information regarding the dpnapy co-ordination mode was deduced by NMR spectroscopy. We have previously used $^{31}P$ NMR spectroscopy to characterize axial and equatorial monophosphine adducts of the parent complex. The axial isomer exhibits the X part of an AMX pattern as a doublet of doublets with two large coupling constants, while the equatorial isomer shows coupling constants which lie in the ranges 120–140 and 5–6 Hz.[9,10]

The $^{31}P$ NMR spectrum of complex **6a** [Fig. 2(*a*)] consists of a doublet of doublets centred at δ −67.5 with coupling constants of 70.5 and 62.0 Hz indicating unambiguously that the dpnapy phosphorus is co-ordinated at the axial site and consequently the molecule is a class I adduct (according to the Andersen description)[14] with a linear Rh–Rh–P moiety. Accordingly the $^{31}P$ NMR resonance falls in the negative region of the spectrum, but its low-frequency shift with respect to those found for the monoadducts $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2L]$ [L = $PPh_3$, $P(C_6H_{11})_3$, or 2-(diphenylphosphino)pyridine][9,10] suggests, according to literature data,[15] that the phosphorus atom is involved in a four-membered chelate ring *via* co-ordination of N(8). Further information on the dpnapy co-ordination mode was deduced from the $^1H$ NMR spectrum which showed four different signals for the methyl groups (δ 2.42, 2.36, 2.16 and 1.89) of the formamidinates, as expected for a molecule having low symmetry, while the dpnapy methyl protons appear at δ 3.01 (2-Me) and 2.60 (4-Me). The downfield shift of the 2-Me protons with respect to free dpnapy (δ 2.62) is a consequence of the magnetic anisotropy of the metal, and indicates that N(1) is also involved in co-ordination.

On the basis of the combined IR and NMR data we suggest the P–N(8) fragment is chelated at one rhodium atom while the N(8)–N(1) fragment adopts a bridging co-ordination mode across the dirhodium core. Such a dpnapy arrangement makes the complex very stable, and attempts to induce axial–equatorial isomerization, on warming its chloroform or acetonitrile solutions have all proven unsuccessful. The reaction pattern leading to complex **6a** could initially involve axial co-ordination of dnapy through the phosphorus atom with formation of a classical monoadduct. This rapidly undergoes ring closure through N(1) and N(8) before isomerization occurs.

Differently from what is observed for $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$, which reacts sequentially with two equivalents of 2-(diphenylphosphino)pyridine, no further

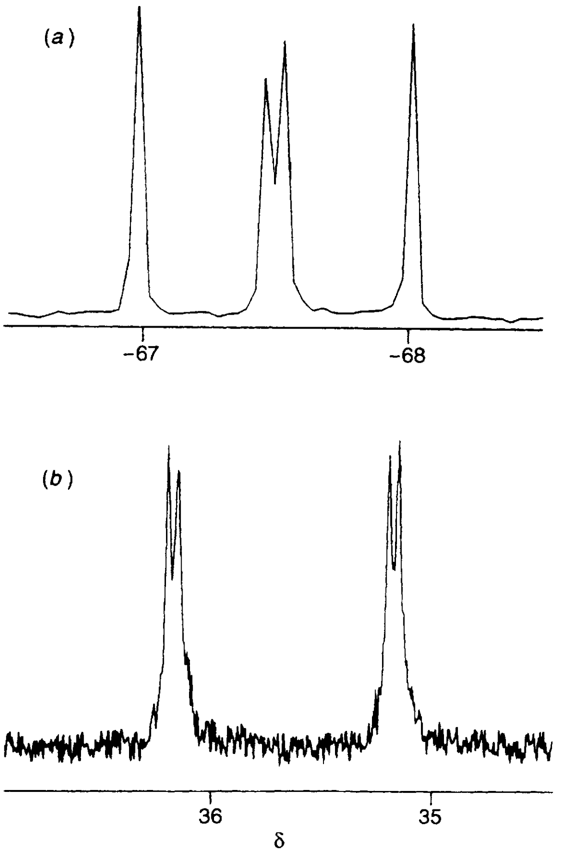
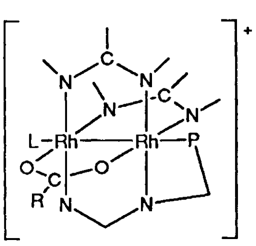
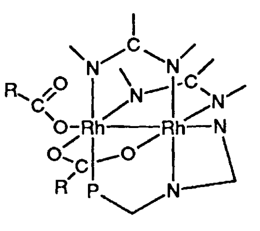


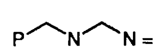
**Fig. 2** The $^{31}P$ NMR spectra (121.496 MHz, $CD_3CN$, 295 K) for complexes **6a** (*a*) and **6b** (*b*)



**6a**



**6b**



= dpnapy, L = MeCN

reaction of **6a** was observed even when an excess of dpnapy was used. Steric more than electronic factors may account for this inertness: the most likely explanation involves unfavourable steric interactions of the incoming phosphorus atom of a second dpnapy with the two *p*-tolyl groups of adjacent formamidinates and the 2-Me group of co-ordinated dpnapy.

When the reaction of $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ with an equivalent of dpnapy is performed under more vigorous conditions (acetonitrile at reflux) a dark red microcrystalline solid is isolated. The identity of this solid, corresponding to the empirical formula $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(dpnapy)]$ **6b**, was established by elemental analysis, molecular weight, conductivity data, and spectroscopic measurements. It is air stable, dissolving easily in benzene and chlorinated solvents to give dark green solutions. The solid-state IR spectrum shows, in the 1600–1700 cm$^{-1}$ region, two distinct absorptions at 1636 and 1673 cm$^{-1}$ indicating that the trifluoroacetate groups are differently co-ordinated. A strong band at 1614 cm$^{-1}$ originating from the C=N naphthyridine skeletal stretching mode is also observed. Molar conductivity measurements show unambiguously that **6b** is non-conducting in non-co-ordinating solvents, while in acetonitrile it undergoes trifluoroacetate dissociation, the molar conductivity being consistent with a 1 : 1 electrolyte. The combined IR and conductivity data lead us to suggest that the solid-state structure involves one trifluoroacetate group bridged across the dirhodium core with the other axially mono-co-ordinated. This structure is very likely retained in poorly co-ordinating solvents while in acetonitrile the species $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)(dpnapy)(MeCN)][CF_3CO_2]$ is generated.

The proton NMR spectrum ($CDCl_3$) resembles that of compound **6a** and the downfield shift of the dpnapy 2-Me proton (δ 3.00) once again suggests that the N(1) atom is involved in co-ordination. In contrast, the $^{31}P$ NMR spectrum [Fig. 2(*b*)] displays a pattern typical of an equatorial phosphorus adduct with a bent Rh–Rh–P fragment: doublet of doublets centred at δ 35.7 with very different coupling constants ($^1J_{Rh-P}$ = 122.1, $^2J_{Rh-P}$ = 5.22 Hz). The geometrical features of dpnapy, characterized by a rigid skeleton constraining the phosphorus and nitrogen atoms in nearly fixed and coplanar positions, prevent its diequatorial co-ordination. On the basis of these considerations we propose for complex **6b** a structure containing the phosphorus atom equatorially bonded to one rhodium and the naphthyridine fragment axially–equatorially chelated to the other.

*Reactions of* $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ *with* exo-*Bidentate Ligands*.—When the starting complex is allowed to react with the *exo*-bidentate ligands 4,4′-bipyridine or pyrazine red-orange insoluble materials, which could not be fully characterized, were obtained. These materials corresponding to the empirical formula $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2L]$ (L = 4,4′-bipy **7** or pyrazine **8**) were easily obtained, as microcrystalline products, by layering a solution of $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ with a solution of the respective ligand dissolved in the same solvent. The same products, which are insoluble in all solvents, can also be obtained by treating the parent complex with $[Ru(NH_3)_5L]^{2+}$ (L = pyrazine or 4,4′-bipy) or in a solid-state reaction simply by mixing the parent complex with the ligand L. The only spectroscopic data available are the $\nu_{asym}(CO_2)$ values which for both the compounds are at 1655 cm$^{-1}$. These materials very likely correspond to one-dimensional linear chains of $Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2$ fragments linked by the ligands L. It is well known that the above ligands lead to the formation of polymeric materials exhibiting in some cases unusual physical properties. Similar structures have been reported for the complexes $[Rh_2(O_2CMe)_4L]$ (L = 2,3,5,6-tetramethylbenzene-1,4-diamine or phenazine).[16]

## Experimental

*General*.—The complex $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(\mu\text{-}O_2CCF_3)_2(H_2O)_2]$ and 7-diphenylphosphino-2,4-dimethyl-1,8-naphthyridine were prepared according to literature procedures.[7a,13] Other reagents and solvents were used as received. The IR spectra were recorded on a Perkin-Elmer FT 43 instrument, $^1H$ and $^{31}P$ NMR spectra on a Bruker AMX 300 spectrometer. Elemental analyses were performed by the Microanalytical Laboratory of the Organic Chemistry Institute of Milan and Analitische Laboratorien Malissa and Reuter, Elbach, West Germany.

*Preparation of Complexes*.—$[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(2,2'\text{-}bipy)]$ **1**. Crude 2,2′-bipyridine (0.018 g, 0.12 mmol) was added to a stirred solution of $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ (0.11 g, 0.12 mmol) in diethyl ether (30 cm$^3$). The solution changed rapidly to red-brown. Stirring was continued for 3 h whereupon a brown precipitate formed. After removal of the solvent *via* syringe, the residue was repeatedly washed with diethyl ether to remove unreacted bipy and crystallized from $CHCl_3$–heptane. Yield 84% (Found: C, 48.60; H, 3.50; F, 10.40; N, 7.50. Calc. for $C_{44}H_{38}$-

$F_6N_6O_4Rh_2{\cdot}CH_2Cl_2$: C, 48.30; H, 3.60; F, 10.15; N, 7.50%). Molar conductivity ($\Omega^{-1}$ cm$^2$ mol$^{-1}$): 250 (MeCN, $10^{-3}$ mol dm$^{-3}$). IR(Nujol mull): $\nu$(NCN) 1582, $\nu_{asym}(CO_2)$ 1642m and 1673s cm$^{-1}$. $^1$H NMR ($CD_3CN$): isomer **a**, $\delta$ 8.96 (d, $J$ = 5, 1 H), 8.86 (d, $J$ = 6.1, 1 H), 8.39 (d, $J$ = 8, 1 H), 8.33 (d, $J$ = 8 Hz, 1 H), 8.1 (m, 2 H) and 7.61 (m, 2 H); isomer **b**, $\delta$ 9.05 (d, $J$ = 5, 2 H), 8.52 (d, $J$ = 8, 2 H), 8.19 (dt, $^1J$ = 8, $^2J$ = 1.3 Hz, 2 H) and 7.71 (m, 2 H).

$[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(\sigma\text{-}O_2CCF_3)_2(2,2'\text{-bipy})_2]$ **2**. 2,2'-Bipyridine (0.2 g, 0.56 mmol) and $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ (0.13 g, 0.14 mmol) were heated at reflux in acetone (30 cm$^3$) for 24 h. During this time the solution changed to red-brown and then was taken to dryness. The solid was washed three times with diethyl ether to remove unreacted bipy and crystallized from $CHCl_3$–heptane. Yield 78% (Found: C, 50.75; H, 3.8; N, 8.70. Calc. for $C_{54}H_{46}F_6N_8O_4Rh_2{\cdot}CHCl_3$: C, 50.40; H, 3.6; N, 8.55%). Molar conductivity ($\Omega^{-1}$ cm$^2$ mol$^{-1}$): 260 (MeCN, $10^{-3}$ mol dm$^{-3}$). IR(Nujol mull): $\nu$(NCN), 1573, $\nu_{asym}(CO_2)$ 1679 cm$^{-1}$. $^1$H NMR ($CD_3CN$): $\delta$ 8.34 (d, $J$ = 5.5, 4 H), 8.18 (t, $J$ = 3.5 Hz, 2 H, CH), 7.85–7.80 (two overlapped multiplets, 8 H) and 7.2 (m, 4 H).

$[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(\sigma\text{-}O_2CCF_3)_2(2,2'\text{-bipy})(C_6H_{11}NC)_2]$ **3**. To a dichloromethane solution of $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(2,2'\text{-bipy})]$ **1** (0.12 g, 0.11 mmol) was added cyclohexyl isocyanide (0.023 g, 0.22 mmol). The solution changed rapidly to red-brown. After stirring for 2 h the solvent was evaporated and the solid crystallized twice from a $CH_2Cl_2$–hexane solution to give a green solid. Yield 90% (Found: C, 54.65; H, 4.8; N, 8.70. Calc. for $C_{58}H_{60}F_6N_8O_4Rh_2$: C, 55.0; H, 4.8; N, 8.9%). Molar conductivity ($\Omega^{-1}$ cm$^2$ mol$^{-1}$): 250 (MeCN, $10^{-3}$ mol dm$^{-3}$). IR(Nujol mull): $\nu$(NCN) 1585, $\nu_{asym}(CO_2)$ 1687, $\nu$(CN) 2170 cm$^{-1}$. $^1$H NMR ($CD_3CN$): $\delta$ 9.16 (d, $J$ = 5.9, 2 H), 8.67 (d, $J$ = 8, 2 H), 8.26 (dt, $^1J$ = 8, $^2J$ = 1.3, 2 H), 8.01 (t, $J$ = 3.2, 2 H, CH) and 7.81 (dt, $^1J$ = 5.9, $^2J$ = 1.5 Hz, 2 H).

$[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(phen)]$ **4**. To a diethyl ether solution of $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ (0.125 g, 0.136 mmol) was added 1,10-phenanthroline (0.024 g, 0.136 mmol). After 4 h the resultant red-brown solution was taken to dryness and the residue crystallized from $CH_2Cl_2$–heptane. Yield 64% (Found: C, 51.20; H, 3.6; N, 7.7. Calc. for $C_{46}H_{38}F_6N_6O_4Rh_2$: C, 52.1; H, 3.6; N, 7.9%). Molar conductivity ($\Omega^{-1}$ cm$^2$ mol$^{-1}$): 260 (MeCN, $10^{-3}$ mol dm$^{-3}$). IR(Nujol mull): $\nu$(NCN) 1556, $\nu_{asym}(CO_2)$ 1644m and 1672s cm$^{-1}$. $^1$H NMR ($CD_3CN$): isomer **a**, $\delta$ 9.23 (d, 1 H), 9.11 (d, 1 H), 8.67 (dd, 1 H), 8.62 (dd, 1 H), 8.15 (s, 1 H) and 8.08 (s, 1 H); isomer **b**, $\delta$ 9.30 (d, $J$ = 4.3, 2 H), 8.77 (dd, $^1J$ = 8.2, $^2J$ = 1.3 Hz, 2 H), 8.20 (s, 2 H) and 7.75 (dd, 2 H).

$[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(\sigma\text{-}O_2CCF_3)_2(phen)_2]$ **5**. To a diethyl ether solution (15 cm$^3$) of $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ (0.12 g, 0.13 mmol) was added solid 1,10-phenanthroline (0.047 g, 0.26 mmol). The reaction mixture immediately changed to red-orange. After 3 h it consisted of a light-brown solid suspended in a light red-orange solution. The solid was filtered off, washed with diethyl ether and dried *in vacuo*. Crystallization from $CHCl_3$–heptane gave red crystals. Yield 68% (Found: C, 54.0; H, 3.44; F, 7.80; N, 8.60. Calc. for $C_{58}H_{46}F_6N_8O_4Rh_2{\cdot}CHCl_3$: C, 54.10; H, 3.60; F, 8.00; N, 8.25%). Molar conductivity ($\Omega^{-1}$ cm$^2$ mol$^{-1}$): 250 (MeCN, $10^{-3}$ mol dm$^{-3}$). IR(Nujol mull): $\nu$(NCN) 1576, $\nu_{asym}(CO_2)$ 1688 cm$^{-1}$. $^1$H NMR ($CD_3CN$): $\delta$ 8.54 (dd, $^1J$ = 5.2, $^2J$ = 1, 4 H), 8.34 (t, $J$ = 3.3, 2 H, CH), 8.15 (dd, $^1J$ = 8.1, $^2J$ = 1 Hz, 4 H), 7.64 (s, 4 H), 7.48 (dd, 4 H) and 2.27 ($CH_3$).

$[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(dpnapy)]$ **6a**. A $CH_2Cl_2$ solution (1 cm$^3$) of dpnapy (0.038 g, 0.110 mmol) was added to a diethyl ether solution (50 cm$^3$) of $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ (0.100 g, 0.109 mmol) and the resulting mixture left to stand for 3 h. During this time compound **6a** precipitated as a dark green microcrystalline solid. It was filtered off, washed with diethyl ether and dried *in vacuo*. Yield 94% (Found: C, 55.15; H, 4.10; F, 9.45; N, 6.85; P, 2.45. Calc. for $C_{56}H_{49}F_6N_6O_4PRh_2$: C, 55.10; H, 4.05; F, 9.35; N, 6.90; P, 2.55%). Molar conductivity ($\Omega^{-1}$ cm$^2$ mol$^{-1}$): 140 (MeCN), 52 ($CH_2Cl_2$) ($5 \times 10^{-4}$ mol dm$^{-3}$). IR: (Nujol mull) $\nu$(NCN) 1572s; $\nu_{asym}(CO_2)$ 1689s and 1636vs; ($CHCl_3$) $\nu_{asym}(CO_2)$ 1688m and 1637vs; (MeCN) $\nu_{asym}(CO_2)$ 1696s and 1639vs cm$^{-1}$. NMR [$CDCl_3$, room temperature (r.t.)]: $^{31}$P-{$^1$H}, $\delta$ −67.5 (dd, $^1J_{Rh-P}$ = 70.5, $^2J_{Rh-P}$ = 62.0 Hz); $^1$H, $\delta$ 3.01 (s, 3 H, 2-Me), 2.60 (s, 3 H, 4-Me) and 2.42, 2.36, 2.16, 1.89 (s, $p$-$MeC_6H_4$).

$[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(dpnapy)]$ **6b**. The complex $[Rh\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ (0.150 g, 0.123 mmol) and dpnapy (0.042 g, 0.123 mmol) were dissolved in MeCN (50 cm$^3$) and the resulting mixture left to reflux for *ca.* 3 h. During this time the initial dark pink solution turned red-brown. After filtration, the solution was taken to dryness and the crude residue recrystallized from $CHCl_3$–$n$-hexane (1:2, 30 cm$^3$) affording dark red microcrystals of **6b**. Yield 80% [Found: C, 55.20; H, 4.10; F, 9.40; N, 6.80; P, 2.50. Calc. for $C_{56}H_{49}F_6N_6O_4PRh_2$: C, 55.10; H, 4.05; F, 9.35; N, 6.90; P, 2.55%. $M$: found ($CHCl_3$) 1195 (calc. 1220.83)]. Molar conductivity ($\Omega^{-1}$ cm$^2$ mol$^{-1}$): 138 (MeCN), 6 ($CH_2Cl_2$) ($10^{-3}$ mol dm$^{-3}$). IR: (Nujol mull) $\nu$(NCN) 1567; $\nu_{asym}(CO_2)$ 1673vs and 1636vs; $\nu$(C=N, dpnapy) 1614s; ($CHCl_3$) $\nu_{asym}(CO_2)$ 1678m and 1636vs; (MeCN) $\nu(CO_2)$ 1696s and 1638vs cm$^{-1}$. NMR ($CDCl_3$, r.t.): $^{31}$P-{$^1$H}, $\delta$ 35.68 (dd, $^1J_{Rh-P}$ = 122.1, $^2J_{Rh-P}$ = 5.22 Hz); $^1$H, $\delta$ 3.00 (s, 3 H, 2-Me), 2.58 (s, 3 H, 4-Me), 2.26, 2.19, 2.12, 1.97 (s, $p$-$MeC_6H_4$).

$[\{Rh_2[CH(NC_6H_4Me\text{-}p)_2]_2(O_2CCF_3)_2(4,4'\text{-bipy})\}_n]$ **7**. This compound was prepared by layering a diethyl ether solution of $[Rh_2\{CH(NC_6H_4Me\text{-}p)_2\}_2(O_2CCF_3)_2(H_2O)_2]$ (0.13 g, 0.14 mmol) with an equimolar quantity of 4,4'-bipyridine dissolved in the same solvent (10 cm$^3$). The initial solution changed from green to red-orange and a red microcrystalline product precipitated. Yield 94% (Found: C, 50.85; H, 3.55; F, 10.90; N, 7.80. Calc. for $C_{44}H_{38}F_6N_6O_4Rh_2$: C, 51.00; H, 3.70; F, 11.0; N, 7.90%). IR(Nujol mull): $\nu_{asym}(CO_2)$ 1655 cm$^{-1}$.

$[\{Rh_2[CH(NC_6H_4Me\text{-}p)_2]_2(O_2CCF_3)_2(pyz)\}_n]$ **8**. The red compound **8** was prepared using the same procedure as for **7** by the use of pyrazine (pyz). Yield 95% (Found: C, 48.00; H, 3.75; F, 12.0; N, 8.85. Calc. for $C_{38}H_{34}F_6N_6O_4Rh_2$: C, 47.60; H, 3.55; F, 11.90; N, 8.75%). IR(Nujol mull): $\nu_{asym}(CO_2)$ 1655 cm$^{-1}$.

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## References

1 T. R. Felthouse, *Prog. Inorg. Chem.*, 1982, **29**, 73; E. B. Boyar and S. D. Robinson, *Coord. Chem. Rev.*, 1983, **50**, 109; F. A. Cotton and R. A. Walton, *Multiple Bonds between Metal Atoms*, Wiley, New York, 1982; H. Brunner, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1183.
2 M. P. Doyle, *Chem. Rev.*, 1986, **86**, 919.
3 L. M. Hall, R. J. Speer and H. J. Ridgway, *J. Clin. Hematol. Oncol.*, 1980, **10**, 25 and refs. therein.
4 P. Piraino, G. Bruno, S. Lo Schiavo, F. Laschi and P. Zanello, *Inorg. Chem.*, 1987, **26**, 2205 and refs. therein.
5 M. P. Doyle, V. Bagheri, T. J. Wandless, N. K. Harn, D. A. Brinker, C. T. Eagle and K. Loh, *J. Am. Chem. Soc.*, 1990, **112**, 1906.
6 M. P. Doyle, R. Pieters, S. F. Martin, R. A. Austin, C. S. Oalmann and P. Muller, *J. Am. Chem. Soc.*, 1991, **113**, 1423; H. Brunner, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1183.
7 (*a*) P. Piraino, G. Bruno, G. Tresoldi, S. Lo Schiavo and P. Zanello, *Inorg. Chem.*, 1987, **26**, 91; (*b*) V. Fimiani, T. Ainis, A. Cavallaro and P. Piraino, *J. Chemother.*, 1990, **2**, 319; (*c*) K. S. Prunik, *Pure Appl. Chem.*, 1989, **61**, 795.
8 S. P. Perlepes, J. C. Huffman, J. H. Matonic, K. R. Dunbar and G. Christou, *J. Am. Chem. Soc.*, 1991, **113**, 2770; C. A. Crawford, J. H. Matonic, W. E. S. Streib, J. C. Huffman, K. R. Dunbar and G. Christou, *Inorg. Chem.*, 1993, **32**, 3125.
9 E. Rotondo, G. Bruno, F. Nicolò, S. Lo Schiavo and P. Piraino, *Inorg. Chem.*, 1991, **30**, 1195.

10 E. Rotondo, E. Mann, P. Piraino and G. Tresoldi, *Inorg. Chem.*, 1989, **28**, 3070.

11 J. M. Casas, R. H. Cayton and M. H. Chisholm, *Inorg. Chem.*, 1991, **30**, 360.

12 (*a*) M. Calligaris, L. Campana, G. Mestroni, M. Tornatore and E. Alessio, *Inorg. Chim. Acta*, 1987, **127**, 103; (*b*) M. A. M. Daniels, N. Mehmet and D. A. Tocher, *J. Chem. Soc., Dalton Trans.*, 1991, 2601.

13 M. Grassi, G. De Munno, F. Nicolò and S. Lo Schiavo, *J. Chem. Soc., Dalton Trans.*, 1992, 2367.

14 G. S. Girolami, V. V. Mainz and R. A. Andersen, *Inorg. Chem.*, 1980, **19**, 805.

15 P. E. Garrou, *Chem. Rev.*, 1981, **81**, 229.

16 F. A. Cotton and T. R. Felthouse, *Inorg. Chem.*, 1981, **20**, 600.

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