Complexes of Rhodium(I) with 1,8-Naphthyridine and Related Ligands. Crystal Structure of $[Rh_2(\mu\text{-napy})_2(nbd)_2][ClO_4]_2\cdot H_2O$ †

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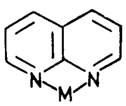
Reactions of stoicheiometric amounts of 1,8-naphthyridine (R-napy) type ligands with $[\{RhCl(diolefin)\}_2]$ or $[Rh(diolefin)(OCMe_2)_x][ClO_4]$ lead to formation of the complexes [RhCl(diolefin)(napy)], $[Rh(diolefin)(2,7Me_2\text{-napy})][ClO_4]$ [diolefin = cyclo-octa-1,5-diene (cod), norborna-2,5-diene (nbd), tetrafluorobenzobarrelene (tfbb), trimethyltetrafluorobenzobarrelene (Me_3tfbb)], $[Rh_2(\mu\text{-R-napy})_2(diolefin)_2][ClO_4]_2\cdot H_2O$ (R = H or 2-Me; diolefin = nbd or tfbb), or $[Rh(cod)(2Me\text{-napy})][ClO_4]$. Mononuclear complexes of the type $[Rh(diolefin)(R\text{-napy})_2][ClO_4]$ are obtained in the presence of an excess of the R-napy ligand. Several tetracarbonyl or dicarbonyl derivatives of formulae $[Rh(napy)_2(CO)_2][ClO_4]$, $[Rh_2(\mu\text{-R-napy})_2(CO)_4][ClO_4]_2$, $[Rh_2(\mu\text{-R-napy})_2(CO)_2(PPh_3)_2][ClO_4]_2$, and $[(diolefin)Rh(\mu\text{-napy})_2Rh(CO)(PPh_3)][ClO_4]_2$ have been prepared from $[Rh(CO)(PPh_3)(OCMe_2)_x][ClO_4]$ or by carbonylation reactions. The structure of $[Rh_2(napy)_2(nbd)_2][ClO_4]_2\cdot H_2O$ has been determined by *X*-ray diffraction methods. Crystals are orthorhombic, space group *Pccn* with $Z = 4$ in a unit cell of dimensions $a = 17.539(11)$, $b = 10.252(7)$, and $c = 17.211(12)$ Å. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.063$ for 1 427 independent observed reflections. The cationic complex $[Rh_2(napy)_2(nbd)_2]^{2+}$, having an imposed symmetry C_2, is binuclear with two napy ligands bridging the two metals. The co-ordination around each Rh atom is completed by a nbd molecule interacting through the two olefin bonds. The distance between the bridged Rh atoms is 2.916(3) Å.

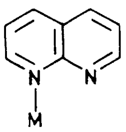
As a continuation of our studies [1-6] on polynuclear rhodium(I) complexes containing bridging nitrogen-donor ligands, we have investigated the chemical and co-ordinative behaviour of the potentially binucleating ligand 1,8-naphthyridine (napy).

In spite of its chelate bite of 2.2 Å,[7] and the unfavourable parallel orientation of the nitrogen lone pairs for chelation, a large number of 1,8-naphthyridine complexes with transition [8] and representative [9] metals has been described having the mode of co-ordination (A). High co-ordination numbers are reached even in complexes of the first-row transition metals such as in $[Fe(napy)_4][ClO_4]_2$.[7] Examples of 1,8-naphthyridine acting as a unidentate ligand (B) are found in the complexes $[AuXMe_2(2,7Me_2\text{-napy})]$ (X = Cl, Br, I, OCN, SCN, SeCN, or CN) [10] and *cis*-$[MCl(napy)(PEt_3)_2][BF_4]$ (M = Pd or Pt),[11] but a fluxional behaviour due to a 1,3-shift of the metal can be observed in solution. The only structural evidence of the binucleating behaviour (C) of the naphthyridine ligand is found in the complexes $[Ni_2Br_2(\mu\text{-napy})_4][BPh_4]$,[12] $[Cu_2(\mu\text{-Cl})Cl_2(\mu\text{-4Me-napy})_2]$,[13] and $[Cu_2(\mu\text{-Cl})_2Cl_2(\mu\text{-napy})_2]$.[14]

Considerable interest has recently been shown in binuclear complexes containing two planar rhodium(I) centres in close proximity, which are linked by a variety of bridging P–P, P–N, or N–N ligands [*i.e.* bis(diphenylphosphino)methane,[15-19] 2-(diphenylphosphino)pyridine,[20] formamidine,[21,22] or triazenide [21,23]]. As far as we know, the only rhodium 1,8-naphthyridine complexes hitherto described are $[RhCl(napy)(CO)_2]$ and $[\{RhCl(CO)_2\}_2(\mu\text{-napy})]$.[24] We report here on some cationic rhodium complexes with 1,8-naphthyridine-type ligands R-napy, where R = H, 2-Me, or 2,7-Me_2.



(A)



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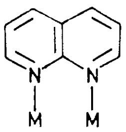

(C)

Results and Discussion

Synthesis and Properties.—Compounds of the type $[\{RhCl(diolefin)\}_2]$ react with 1,8-naphthyridine (napy) in dichloromethane yielding air-stable yellow microcrystalline complexes [RhCl(diolefin)(napy)] [diolefin = cyclo-octa-1,5-diene (cod) (1), norborna-2,5-diene (nbd) (2), or tetrafluorobenzobarrelene ‡ (tfbb) (3)]. These complexes are non-electrolytes in acetone and their molecular weights (Table 1), in solution, correspond to mononuclear species where the 1,8-naphthyridine should act as a unidentate ligand due to the low tendency of diolefin–rhodium(I) complexes to become five-co-ordinated.

Addition of an excess of 1,8-naphthyridine to acetone solutions of the complexes (1)—(3) leads to the formation of ionic species according to equation (1). Conductivity measurements on the cyclo-octa-1,5-diene system show that the extent of formation of the cationic species is very low. Nevertheless, cationic complexes of the formula $[Rh(diolefin)(napy)_2][ClO_4]$ (4)—(7) can be isolated from the solutions by addition of sodium perchlorate. Alternatively, these complexes and some analogous $[Rh(diolefin)(R\text{-napy})_2][ClO_4]$ (9)—(11)

$$[RhCl(diolefin)(napy)] + napy \longrightarrow [Rh(diolefin)(napy)_2]^+ + Cl^- \qquad (1)$$

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† Bis(μ-1,8-naphthyridine-*NN'*)-bis[(η-norborna-2,5-diene)-rhodium(I)](*Rh–Rh*) diperchlorate monohydrate.

Supplementary data available (No. SUP 23740, 12 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

‡ Systematic names: tfbb = tetrafluorobenzo[5,6]bicyclo[2.2.2]octa-2,5,7-triene; Me_3tfbb = 1,3,8-trimethyl(tetrafluorobenzo[5,6])bicyclo-[2.2.2]octa-2,5,7-triene.

Table 1. Colour, analytical, conductance, molecular weight, yield, and spectroscopic data for the new complexes

Compound	Colour	Analysis (%)[a] C	H	N	Λ_M[b]	B[c]	Yield (%)	$\tilde{\nu}$(CO)/cm^{-1}	U.v. absorption, $\lambda_{max.}$/nm
(1) [RhCl(cod)(napy)][d]	Yellow	50.4 (51.0)	4.85 (4.80)	7.20 (7.45)	1		97		
(2) [RhCl(nbd)(napy)][e]	Yellow	49.65 (49.95)	4.05 (3.90)	8.30 (7.75)			64		
(3) [RhCl(tfbb)(napy)][f]	Yellow	48.7 (48.55)	2.65 (2.45)	5.80 (5.65)			59		
(4) [Rh(cod)(napy)$_2$][ClO$_4$]	Orange	50.0 (50.5)	4.05 (4.25)	9.65 (9.80)	83[g]		93		
(5) [Rh(nbd)(napy)$_2$][ClO$_4$]	Orange	49.4 (49.8)	3.85 (3.65)	10.0 (10.1)	91[g]		93		
(6) [Rh(tfbb)(napy)$_2$][ClO$_4$]	Yellow	49.15 (48.8)	3.00 (2.65)	8.10 (8.15)	136		90		
(7) [Rh(Me$_3$tfbb)(napy)$_2$][ClO$_4$]	Yellow	50.75 (50.95)	3.75 (3.30)	7.55 (7.65)	135		46		
(8) [Rh(napy)$_2$(CO)$_2$][ClO$_4$]	Yellow	41.5 (41.7)	2.80 (2.35)	10.1 (10.8)	123		98	2 100, 2 030[h]	
(9) [Rh(cod)(2Me-napy)$_2$][ClO$_4$]	Orange	51.25 (52.15)	4.70 (4.70)	9.35 (9.35)	95[g]		84		
(10) [Rh(nbd)(2Me-napy)$_2$][ClO$_4$]	Orange	51.45 (51.5)	4.20 (4.15)	9.25 (9.60)	95[g]		87		
(11) [Rh(nbd)(2,7Me$_2$-napy)$_2$][ClO$_4$]	Yellow	53.0 (53.1)	5.05 (4.60)	9.05 (9.15)	145		84		
(12) [Rh(cod)(2Me-napy)][ClO$_4$]	Yellow	44.8 (44.9)	4.45 (4.45)	6.30 (6.15)	88[g]	186	86		
(13) [Rh(cod)(2,7Me$_2$-napy)][ClO$_4$]	Yellow	46.2 (46.1)	4.65 (4.75)	5.60 (5.95)	93[g]	232	84		
(14) [Rh(nbd)(2,7Me$_2$-napy)][ClO$_4$]	Yellow	45.5 (45.1)	3.80 (4.00)	6.45 (6.20)	154		73		
(15) [Rh(Me$_3$tfbb)(2,7Me$_2$-napy)][ClO$_4$]	Yellow	47.7 (47.75)	4.15 (3.50)	4.20 (4.45)	141		86		
(16) [Rh$_2$(μ-napy)$_2$(nbd)$_2$][ClO$_4$]$_2$·H$_2$O	Dark purple	41.7 (41.55)	3.25 (3.70)	6.65 (6.55)	188[g]	348	85		503
(17) [Rh$_2$(μ-napy)$_2$(tfbb)$_2$][ClO$_4$]$_2$·H$_2$O	Red	42.75 (42.3)	2.80 (2.30)	5.00 (4.95)	174[g]	421	95		496
(18) [Rh$_2$(μ-napy)$_2$(CO)$_4$][ClO$_4$]$_2$·H$_2$O	Red	29.55 (30.2)	1.65 (1.75)	7.15 (7.05)	160[g]	385	98	2 115, 2 095, 2 055,[i] 1 995, 1 980[i]	476
(19) [Rh$_2$(μ-napy)$_2$(CO)$_2$(PPh$_3$)$_2$][ClO$_4$]$_2$·H$_2$O	Brown	51.45 (51.35)	3.70 (3.50)	4.60 (4.45)	176[g]	405	85	2 020, 1 995[h]	465
(20) [Rh$_2$(μ-2Me-napy)$_2$(nbd)$_2$][ClO$_4$]$_2$·H$_2$O	Purple	43.3 (42.95)	3.65 (3.85)	6.30 (6.25)	210[g]	346	94		537, 480
(21) [Rh$_2$(μ-2Me-napy)$_2$(tfbb)$_2$][ClO$_4$]$_2$·H$_2$O	Red	43.65 (43.35)	3.05 (2.60)	4.70 (4.80)	190[g]	368	97		518
(22) [Rh$_2$(μ-2Me-napy)$_2$(CO)$_4$][ClO$_4$]$_2$	Red	32.45 (32.8)	2.00 (2.00)	7.10 (6.95)	194[g]	347	90	2 110, 2 080, 2 040[i]	483
(23) [Rh$_2$(μ-2Me-napy)$_2$(CO)$_2$(PPh$_3$)$_2$][ClO$_4$]$_2$	Brown	52.5 (52.8)	4.05 (3.65)	4.30 (4.40)	180[g]	291	63	2 000—1 990[i]	490
(24) [(nbd)Rh(μ-napy)$_2$Rh(CO)(PPh$_3$)][ClO$_4$]$_2$·H$_2$O	Dark purple	47.3 (47.35)	3.75 (3.50)	5.25 (5.25)	186[g]	389	68	2 005[i]	
(25) [(tfbb)Rh(μ-napy)$_2$Rh(CO)(PPh$_3$)][ClO$_4$]$_2$·H$_2$O	Dark purple	47.45 (47.05)	3.35 (2.95)	4.55 (4.65)	176[g]	338	68	2 005[i]	

[a] Calculated values are given in parentheses. [b] In acetone unless stated otherwise. [c] From $\Lambda_c = \Lambda_o - B\sqrt{c}$. [d] M 380 (calc. 377). [e] M 345 (calc. 361). [f] M 491 (calc. 495). [g] In nitromethane. [h] In CH$_2$Cl$_2$. [i] In Nujol.

compounds can be prepared from an excess of the ligand R-napy (R-napy = 1,8-naphthyridine, 2-methyl-1,8-naphthyridine, or 2,7-dimethyl-1,8-naphthyridine) with the cationic species $[Rh(diolefin)(OCMe_2)_x][ClO_4]$.[25] Complexes (4)—(7) and (9)—(11) are isolated as air-stable yellow or orange microcrystalline solids and show characteristic i.r. absorptions of the co-ordinated diolefin and 1,8-naphthyridine ligands along with bands due to the unco-ordinated perchlorate anion at *ca.* 1 100 and 620 cm^{-1}. They behave as 1 : 1 electrolytes in acetone. The rhodium atom is probably in a square-planar environment where the 1,8-naphthyridine ligands are co-ordinated to the metal through only one of the nitrogen atoms as in (B).

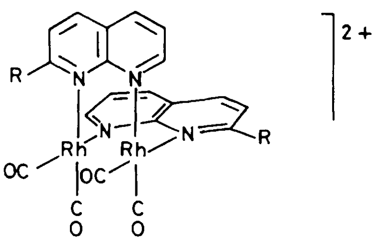
Bubbling of carbon monoxide through a dichloromethane solution of $[Rh(cod)(napy)_2][ClO_4]$ leads to the formation of $[Rh(napy)_2(CO)_2][ClO_4]$ (8) which is isolated as a yellow solid contaminated with traces of a red complex $[Rh_2(\mu\text{-}napy)_2(CO)_4][ClO_4]_2$. Nevertheless, recrystallization of this solid in the presence of free 1,8-naphthyridine renders pure complex (8) which exhibits two ν(CO) bands in the 2 100—2 000 cm^{-1} region characteristic of *cis*-dicarbonylrhodium complexes. Similarly complexes (1)—(3) react with carbon monoxide leading to the displacement of the co-ordinated diolefin and formation of $[RhCl(napy)(CO)_2]$. The analogous complexes $[IrCl(cod)(napy)]$ and $[IrCl(napy)(CO)_2]$ can be prepared by similar methods starting from $[\{IrCl(cod)\}_2]$, and have been identified by standard analytical and spectroscopic techniques.

Addition of stoicheiometric amounts (1 : 1) of R-napy (R = H, 2-Me, or 2,7-Me_2) to the species $[Rh(diolefin)(OCMe_2)_x]^+$ results in the formation of yellow mononuclear complexes for R = 2,7-Me_2 of formula $[Rh(diolefin)(2,7\text{-}Me_2\text{-}napy)][ClO_4]$ (13)—(15) but binuclear red or purple compounds $[Rh_2(\mu\text{-}R\text{-}napy)_2(diolefin)_2][ClO_4]_2$ are obtained for R = H or 2-Me and diolefin = nbd or tfbb [(16), (17), (20), and (21)]. However, the related complex $[Rh(cod)(2Me\text{-}napy)][ClO_4]$ (12) is mononuclear. Complexes (12)—(15) are 1 : 1 electrolytes in acetone or nitromethane. Conductivity studies on nitromethane solutions of complexes (12) and (13) at different concentrations give slopes for the Onsager equation characteristic [26] of 1 : 1 electrolytes. In these mononuclear complexes the 1,8-naphthyridine-type ligand should act in the bidentate mode (A).

Bubbling carbon monoxide through dichloromethane suspensions of the binuclear complexes (16) or (20) gives rise to the tetracarbonyl derivatives $[Rh_2(\mu\text{-}R\text{-}napy)_2(CO)_4][ClO_4]_2$ [R = H (18) or 2-Me (22)]. It seems noteworthy that the binuclear complex (22) is also formed by carbonylation of the mononuclear cyclo-octa-1,5-diene complex $[Rh(cod)(2Me\text{-}napy)][ClO_4]$. The i.r. spectra of (18) and (22) in the carbonyl region show, in each case, three absorptions in accord with the C_{2v} or approximately C_{2v} symmetry of the proposed structures. A similar structure has been proposed by Connelly *et al.*[21] for the related neutral $[\{Rh(RNXNR)(CO)_2\}_2]$ (X = N or CMe) complexes.

Complexes (18) and (22) undergo carbonyl-substitution reactions with triphenylphosphine at room temperature in dichloromethane giving $[Rh_2(\mu\text{-}R\text{-}napy)_2(CO)_2(PPh_3)_2][ClO_4]_2$ [R = H (19) or 2-Me (23)] respectively. Complex (19) shows two strong i.r. ν(CO) bands, but only a broad ν(CO) band is observed for complex (23) suggesting a $[(Ph_3P)(OC)Rh(\mu\text{-}R\text{-}napy)_2Rh(CO)(PPh_3)]^{2+}$ disposition. An alternative and more convenient preparation of complexes (19) and (23) involves the reaction of the species $[Rh(CO)(PPh_3)(OCMe_2)_x]^+$ with the appropriate 1,8-naphthyridine ligand.

Complexes (4)—(11) still have two unco-ordinated nitrogen atoms, one from each 1,8-naphthyridine ligand, and these ligands potentially could act as bidentate ligands. In fact, the complex $[Rh(nbd)(napy)_2][ClO_4]$ reacts with $[Rh(nbd)(OCMe_2)_x]^+$ affording the binuclear complex (16). Reaction of complex (5) or (6) with $[Rh(CO)(PPh_3)(OCMe_2)_x]^+$ gives the binuclear complexes $[(diolefin)Rh(\mu\text{-}napy)_2Rh(CO)(PPh_3)][ClO_4]_2$ [diolefin = nbd (24) or tfbb (25)] respectively. Nevertheless a redistribution of the napy ligands occurs in the reactions of complexes (5), (6), and (10) with the solvated species $[Rh(Me_3tfbb)(OCMe_2)_x]^+$ or $[Rh(cod)(OCMe_2)_x]^+$ affording the binuclear complexes (16), (17), or (20) respectively and yellow uncharacterizable oils which are probably mononuclear complexes.



(18) R = H

(22) R = Me

The binuclearity of the above complexes was established by conductance measurements in nitromethane at different concentrations (3×10^{-3}—4×10^{-4} mol dm^{-3}). The calculated values for B from the Onsager law ($\Lambda_e = \Lambda_0 - B\sqrt{c}$) (Table 1) agree with this formulation. Nevertheless some dissociation occurs in the most dilute samples, especially for complex (23). These compounds generally crystallize with a molecule of water (see *X*-ray structure), probably originating in the acetone solvent. In fact, bands at *ca.* 3 600 and 1 630 cm^{-1} are observed in the i.r. spectra of these complexes.

The electronic spectra of the binuclear complexes exhibit a very strong band in the visible region, associated with their intense colours, with molar absorption coefficients higher than 2×10^3 dm^3 mol^{-1} cm^{-1}. They do not follow the Lambert–Beer law in the range of concentrations used (around 10^{-4} mol dm^{-3}) due to dissociation. The intense colour of some binuclear rhodium(I) complexes has been attributed to a pronounced shift of a d_{z^2}–π^* metal-to-ligand transition to lower energies, which is sensitive to the separation between the metal centres and the relative orientation of the co-ordination planes.[27] The position of this band in the complexes described here suggests that the rhodium atoms are in close proximity. In order to confirm the binucleating ability of the 1,8-naphthyridine ligand and the Rh–Rh intramolecular distance the structure of complex (16) was solved by *X*-ray methods.

Description of the Structure of $[Rh_2(\mu\text{-}napy)_2(nbd)_2][ClO_4]_2\cdot H_2O$.—The crystal structure consists of binuclear cations $[Rh_2(\mu\text{-}napy)_2(nbd)_2]^{2+}$, perchlorate anions, and water of crystallization. A view of the cation with the atomic numbering scheme is given in Figure 1. Selected bond distances and angles are given in Table 2. The cation, which has an imposed crystallographic C_2 symmetry, is binuclear with two 1,8-naphthyridine ligands bridging the two metals through the N atoms; the co-ordination around each Rh atom is completed by a norbornadiene molecule interacting through the two olefin bonds. If M(1) and M(2) are the midpoints of the C(9)—C(10) and C(12)–C(13) bonds, the Rh–M(1) and Rh–M(2) distances are 1.98(2) and 1.99(2) Å. The rhodium has a slightly distorted square-planar environment, the deviations of M(1), M(2), N(1), and N(2^1) from the mean plane passing through them being 0.05(2), −0.05(2), −0.02(1), and 0.02(1) Å with the rhodium atom out of this plane by 0.19(1) Å. The Rh–N bond distances [2.12(1) and 2.15(1) Å] are comparable

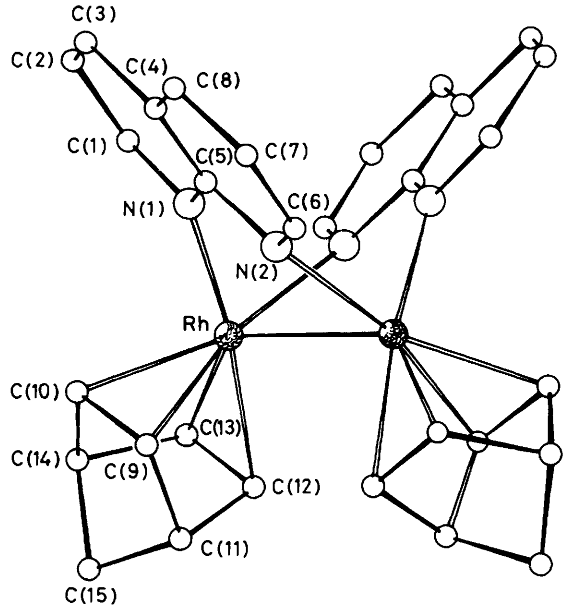


Figure 1. View of the cation $[Rh_2(\mu\text{-napy})_2(nbd)_2]^{2+}$ with the atomic numbering scheme

with those reported for complexes with ligands containing two nitrogen atoms bridging two Rh metals [*e.g.* pyrazolate,[1,3] imidazolate,[4] bi-imidazolate (bim),[28,29] and 2,2′-bibenzimidazolate [6]]. Also the Rh–C bond distances (2.09—2.13 Å) involving the nbd ligand are quite regular if compared with other bond distances involving the same ligand [30] or ligands having a very similar behaviour such as cyclo-octa-1,5-diene.[6,28] Both co-ordinated double bonds, C(9)–C(10) and C(12)–C(13), have lengths of 1.45(3) Å, longer than in free nbd (1.338 Å),[31] as expected.

The 1,8-naphthyridine ligand presents no peculiar structural features if compared with the few other napy complexes reported.[12–14] It is nearly planar, deviations of N(1), C(1), C(2), C(3), C(4), C(5), N(2), C(6), C(7), and C(8) from the mean plane passing through them being 0.03(1), −0.03(2), −0.03(2), 0.01(2), 0.04(2), −0.01(2), 0.01(1), −0.02(2), 0.01(2), and −0.01(2) Å respectively.

The distance between the bridged rhodium atoms is short [2.916(3) Å]. Shorter distances between copper atoms have been found in two napy dimeric complexes,[13,14] but single or double Cl bridges were also present. Rhodium–rhodium separations ranging from 2.612 to 2.841 Å have been found in several binuclear complexes with dicarbonyl or $Ph_2PCH_2PPh_2$ bridges; [19,20] these distances were considered indicative of the presence of a metal–metal bond. A Rh–Rh separation of 2.975(1) Å has been found in the tetranuclear $[Rh_4(CO)_8(bim)_2]$ complex [29] and the presence of a metal–metal interaction was postulated. In the present case a metal–metal interaction can be confirmed by the deviation of the metal from square co-ordination towards the other metal atom, so the co-ordination about each rhodium could be described more precisely as five-co-ordinate with the other rhodium atom occupying the fifth co-ordination site of each square plane.

Figure 2 shows the crystal packing, which involves no hydrogen bonding.

Conclusions

In summary, this study on rhodium(I) complexes has shown that the naphthyridine moiety can behave as a bidentate ligand (A) creating a four-membered chelate ring, as a unidentate ligand (B), or as a binucleating ligand (C) with the rhodium atoms in close proximity. Interestingly, no binuclear rhodium(I) complexes with either $2,7Me_2$-napy or cyclo-octa-1,5-diene have been detected. Furthermore, carbonylation of the mononuclear complex $[Rh(cod)(2Me\text{-napy})][ClO_4]$ affords the binuclear derivative $[Rh_2(\mu\text{-}2Me\text{-napy})_2(CO)_4][ClO_4]_2$.

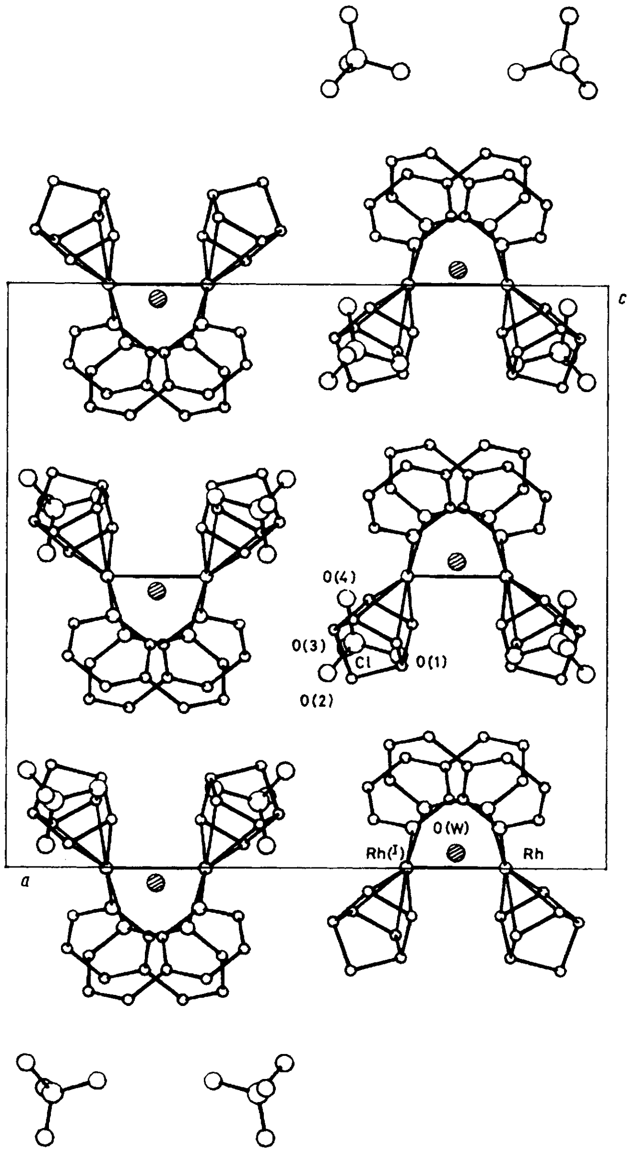


Figure 2. Projection of the structure of $[Rh_2(\mu\text{-napy})_2(nbd)_2][ClO_4]_2{\cdot}H_2O$ along *b* showing the packing of the cations, perchlorate anions, and water molecules

Experimental

Measurements.—Elemental analyses were carried out with a Perkin-Elmer 240B microanalyzer. Infrared spectra (range 4 000—200 cm^{-1}) were recorded on a Perkin-Elmer 599 spectrophotometer using Nujol mulls between polyethylene sheets or dichloromethane solutions in NaCl windows. Conductivities were measured in *ca.* 5×10^{-4} mol dm^{-3} acetone or nitromethane solutions, unless otherwise stated,

Table 2. Bond distances (Å) and angles (°) *

(*a*) In the rhodium co-ordination sphere

Rh–N(1)	2.12(1)	N(1)–Rh–N(2^{I})	87.9(5)	N(2^{I})–Rh–C(10)	151.5(6)	C(10)–Rh–C(12)	81.1(7)
Rh–N(2^{I})	2.15(1)	N(1)–Rh–C(9)	99.6(6)	N(2^{I})–Rh–C(12)	105.8(6)	C(10)–Rh–C(13)	67.9(7)
Rh–C(9)	2.09(2)	N(1)–Rh–C(10)	90.0(6)	N(2^{I})–Rh–C(13)	99.2(6)	C(12)–Rh–C(13)	40.0(7)
Rh–C(10)	2.13(2)	N(1)–Rh–C(12)	164.9(6)	C(9)–Rh–C(10)	40.3(8)		
Rh–C(12)	2.11(2)	N(1)–Rh–C(13)	145.5(6)	C(9)–Rh–C(12)	65.8(7)		
Rh–C(13)	2.13(2)	N(2^{I})–Rh–C(9)	166.9(7)	C(9)–Rh–C(13)	80.8(7)		

(*b*) In the napy and nbd ligands

N(1)–C(1)	1.32(3)	C(1)–N(1)–C(5)	117(2)	C(10)–C(9)–C(11)	106(2)
C(1)–C(2)	1.39(3)	Rh–N(1)–C(1)	113(1)	C(10)–C(9)–Rh	71(1)
C(2)–C(3)	1.41(3)	Rh–N(1)–C(5)	129(1)	C(11)–C(9)–Rh	99(1)
C(3)–C(4)	1.44(3)	N(1)–C(1)–C(2)	125(2)	C(9)–C(10)–C(14)	103(2)
C(4)–C(5)	1.37(2)	C(1)–C(2)–C(3)	118(2)	C(9)–C(10)–Rh	69(1)
N(1)–C(5)	1.33(2)	C(2)–C(3)–C(4)	117(2)	C(14)–C(10)–Rh	96(1)
C(5)–N(2)	1.39(2)	C(3)–C(4)–C(5)	118(2)	C(11)–C(12)–C(13)	106(1)
C(6)–N(2)	1.33(2)	C(3)–C(4)–C(8)	118(1)	C(11)–C(12)–Rh	97(1)
C(6)–C(7)	1.35(3)	C(5)–C(4)–C(8)	123(2)	C(13)–C(12)–Rh	71(1)
C(7)–C(8)	1.44(3)	C(4)–C(5)–N(1)	124(2)	C(14)–C(13)–C(12)	105(1)
C(4)–C(8)	1.36(3)	C(4)–C(5)–N(2)	120(2)	C(14)–C(13)–Rh	98(1)
C(9)–C(10)	1.45(3)	N(1)–C(5)–N(2)	116(1)	C(12)–C(13)–Rh	69(1)
C(12)–C(13)	1.45(3)	C(5)–N(2)–C(6)	117(1)	C(15)–C(11)–C(12)	102(2)
C(10)–C(14)	1.60(3)	C(5)–N(2)–Rh(^{I})	124(1)	C(15)–C(11)–C(9)	106(2)
C(9)–C(11)	1.50(3)	C(6)–N(2)–Rh(^{I})	116(1)	C(12)–C(11)–C(9)	98(1)
C(13)–C(14)	1.55(3)	N(2)–C(6)–C(7)	125(2)	C(10)–C(14)–C(13)	98(1)
C(11)–C(12)	1.52(3)	C(6)–C(7)–C(8)	118(2)	C(10)–C(14)–C(15)	103(2)
C(14)–C(15)	1.54(3)	C(7)–C(8)–C(4)	117(2)	C(13)–C(14)–C(15)	102(2)
C(11)–C(15)	1.55(3)			C(11)–C(15)–C(14)	93(1)

(*c*) In the perchlorate anion

Cl–O(1)	1.43(2)	O(1)–Cl–O(2)	100(1)	O(2)–Cl–O(3)	110(1)
Cl–O(2)	1.40(2)	O(1)–Cl–O(3)	115(1)	O(2)–Cl–O(4)	115(1)
Cl–O(3)	1.36(2)	O(1)–Cl–O(4)	110(1)	O(3)–Cl–O(4)	107(1)
Cl–O(4)	1.35(3)				

* Equivalent position: I $\frac{1}{2} - x, \frac{1}{2} - y, z$.

using a Philips 9501/01 conductimeter. Molecular weights were determined with a Hitachi–Perkin-Elmer 115 osmometer using chloroform solutions. Visible–ultraviolet spectra were run on a Cary 17 spectrophotometer on acetone solutions of the complexes (range 700—330 nm).

Syntheses.—The reactions were carried out at room temperature with 0.1—0.3 mmol of starting materials. Prior to use, solvents were purified by standard methods. The compounds [{RhCl(diolefin)}$_2$] (diolefin = cod,[32] nbd,[33] tfbb,[34] or Me$_3$tfbb [34]), [Rh(CO)(PPh$_3$)(OCMe$_2$)$_x$][ClO$_4$],[35] 1,8-naphthyridine,[36] 2-methyl-1,8-naphthyridine,[8d] and 2,7-dimethyl-1,8-naphthyridine [8d] were prepared according to literature methods.

[RhCl(diolefin)(napy)] (1)—(3). Solid 1,8-naphthyridine (13 mg, 0.1 mmol) was mixed with solutions of the complexes [{RhCl(diolefin)}$_2$] (diolefin = cod, nbd, or tfbb) (0.05 mmol) in dichloromethane (5 cm^3). Concentration of these solutions to *ca.* 1 cm^3 and slow addition of hexane (10 cm^3) rendered the complexes (1)—(3) as crystals, which were filtered off, washed with hexane, and then vacuum-dried.

[Rh(diolefin)(R-napy)$_2$][ClO$_4$] (4)—(7) *and* (9)—(11). *Method A*. A mixture of the complex [{RhCl(diolefin)}$_2$] (diolefin = cod, tfbb, or Me$_3$tfbb) (0.1 mmol), 1,8-naphthyridine (65 mg, 0.5 mmol), and Na[ClO$_4$]·H$_2$O (28 mg, 0.2 mmol) in methanol (10 cm^3) was stirred for 30 min. The solvent was pumped off, the residue extracted with dichloromethane (20 cm^3) and then filtered. Concentration of the filtrate to *ca.* 1 cm^3 and addition of hexane (10 cm^3) gave complexes (4), (6), and (7) as crystals which were filtered off, washed with diethyl ether, and vacuum-dried.

Method B. An acetone solution (15 cm^3) of [Rh(diolefin)(OCMe$_2$)$_x$]$^+$ (diolefin = cod, nbd, tfbb, or Me$_3$tfbb) (prepared by treating the appropriate [{RhCl(diolefin)}$_2$] (0.1 mmol) with Ag[ClO$_4$] (42 mg, 0.2 mmol) in acetone for 30 min and filtering off the AgCl formed) was added to a solution of 1,8-naphthyridine, 2-methyl-1,8-naphthyridine, or 2,7-dimethyl-1,8-naphthyridine (0.40 mmol) in acetone. Evaporation of the solutions to *ca.* 1 cm^3 and addition of hexane (10 cm^3) gave complexes (4)—(7) and (9)—(11) as crystals which were filtered off, washed with diethyl ether, and then vacuum-dried.

Reaction of complex (4) *with carbon monoxide*. Dry carbon monoxide was bubbled through a dichloromethane solution (5 cm^3) of complex (4) (100 mg, 0.19 mmol) for 15 min. Solid 1,8-naphthyridine (10 mg) was added to the resulting yellow solution. Addition of diethyl ether resulted in crystallization of the complex [Rh(napy)$_2$(CO)$_2$][ClO$_4$] (8) which was filtered off, washed with diethyl ether, and vacuum-dried.

[Rh(diolefin)(R-napy)][ClO$_4$] (12)—(15). An acetone solution of [Rh(diolefin)(OCMe$_2$)$_x$]$^+$ (0.15 mmol in 15 cm^3) (prepared as described above) was added to a solution of 2,7-dimethyl-1,8-naphthyridine (0.15 mmol). Evaporation of the resulting solutions to *ca.* 1 cm^3 and addition of diethyl ether (10—20 cm^3) gave complexes (13)—(15) as crystals which were filtered off, washed with diethyl ether, and vacuum-dried. Complex (12) was similarly prepared starting from [Rh(cod)(OCMe$_2$)$_x$][ClO$_4$] and 2Me-napy.

Reaction of complex (12) *with carbon monoxide.* Dry carbon monoxide was bubbled through a solution of complex (12) (35 mg, 0.07 mmol) in dichloromethane (5 cm^3) for 30 min. The colour of the solution turned deep red and dark red crystals of complex $[Rh_2(\mu\text{-}2Me\text{-}napy)_2(CO)_4][ClO_4]_2$ (22) precipitated. Diethyl ether (5 cm^3) was added to complete the precipitation, which is almost quantitative. The solid was filtered off, washed with diethyl ether, and vacuum-dried.

$[Rh_2(\mu\text{-}R\text{-}napy)_2(diolefin)_2][ClO_4]_2{\cdot}H_2O$ (16), (17), (20), *and* (21). A solution of $[Rh(diolefin)(OCMe_2)_x]^+$ (diolefin = nbd or tfbb) (0.30 mmol) in acetone (15 cm^3) (prepared as described above) was added to an acetone solution of 1,8-naphthyridine or 2-methyl-1,8-naphthyridine (0.30 mmol in 10 cm^3). Near to the end of the addition the colour of the solution turned deep red. Evaporation of these solutions to *ca.* 2 cm^3 and addition of diethyl ether (10 cm^3) rendered the complexes (16), (17), (20), and (21) as crystals. These were filtered off, washed with diethyl ether, and vacuum-dried. The complexes crystallize with one molecule of water.

$[Rh_2(\mu\text{-}R\text{-}napy)_2(CO)_4][ClO_4]_2$ (18) *and* (22). Carbon monoxide was bubbled through a suspension of complex (16) or (20) (0.2 mmol) in dichloromethane (15 cm^3) for 30 min or 1 h respectively. The precipitation of complex (22) was completed by addition of diethyl ether (15 cm^3). The solids were filtered off, washed with diethyl ether and then hexane, and vacuum-dried. Complex (18) crystallizes with one molecule of water and both decompose slowly on storage. **CAUTION:** Old samples exploded violently in the microanalyzer.

$[Rh_2(\mu\text{-}R\text{-}napy)_2(CO)_2(PPh_3)_2][ClO_4]_2$ (19) *and* (23). A solution of $[Rh(CO)(PPh_3)(OCMe_2)_x][ClO_4]$ (0.2 mmol) in acetone (15 cm^3) was added to an acetone solution (10 cm^3) of 1,8-naphthyridine or 2-methyl-1,8-naphthyridine (0.2 mmol). The resulting solution was evaporated to *ca.* 2 cm^3 yielding brown solids. The precipitation was completed by addition of either hexane [10 cm^3, complex (19)] or dichloromethane [2 cm^3, complex (23)]. The solids were filtered off, washed with diethyl ether, and vacuum-dried. Complex (19) crystallizes with one molecule of water.

$[(diolefin)Rh(\mu\text{-}napy)_2Rh(CO)(PPh_3)][ClO_4]_2{\cdot}H_2O$ (24) *and* (25). An acetone solution (10 cm^3) of $[Rh(CO)(PPh_3)(OCMe_2)_x][ClO_4]$ (0.07 mmol) was added to the complex $[Rh(nbd)(napy)_2][ClO_4]$ or $[Rh(tfbb)(napy)_2][ClO_4]$ (0.07 mmol) in acetone (5 cm^3), giving a purple solution. This was concentrated to *ca.* 2 cm^3 and diethyl ether (10 cm^3) added to complete the crystallization of a dark purple solid. The crystals were filtered off, washed with methanol (1 cm^3) and then with diethyl ether, and vacuum-dried.

Redistribution reactions. Acetone solutions (10 cm^3) of the solvated species $[Rh(diolefin)(OCMe_2)_x]^+$ (diolefin = cod or Me_3tfbb) (0.05 mmol) were added to solutions of complex (5), (6), or (10) (0.05 mmol) in acetone (5 cm^3). The resulting purple or red solutions were evaporated to dryness and the residue extracted with dichloromethane (3 cm^3) leaving complex (16), (17), or (20) in suspension and a reddish solution. The solids were filtered off, washed with diethyl ether, and air-dried. Diethyl ether (10 cm^3) was added then to the filtrate to complete the precipitation of complex (16), (17), or (20).

X-Ray Crystal Structure Analysis of Complex (16).—Single crystals suitable for *X*-ray diffraction studies were grown by slow evaporation of an acetone solution of complex (16). A bipyramidal crystal with dimensions *ca.* 0.25 × 0.25 × 0.30 mm was used for data collection. The unit-cell parameters were refined by a least-squares procedure applied to the θ values of 29 reflections accurately measured on a Siemens AED single-crystal diffractometer.

Table 3. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses for the non-hydrogen atoms

Atom	*X/a*	*Y/b*	*Z/c*
Rh	1 674(1)	2 341(1)	12(1)
Cl	4 210(3)	−2 860(5)	3 865(3)
N(1)	1 970(9)	1 277(14)	1 025(9)
N(2)	3 226(8)	904(13)	692(8)
C(1)	1 391(15)	1 104(24)	1 506(13)
C(2)	1 381(13)	214(20)	2 118(11)
C(3)	2 044(11)	−519(18)	2 259(12)
C(4)	2 683(11)	−294(15)	1 749(8)
C(5)	2 612(11)	640(16)	1 181(10)
C(6)	3 877(12)	273(18)	829(11)
C(7)	3 975(13)	−644(20)	1 385(14)
C(8)	3 348(12)	−923(18)	1 898(11)
C(9)	1 756(12)	849(18)	−815(11)
C(10)	1 038(11)	715(18)	−400(11)
C(11)	1 587(12)	1 634(19)	−1 530(11)
C(12)	1 496(10)	2 963(18)	−1 143(11)
C(13)	772(11)	2 915(15)	−740(10)
C(14)	455(11)	1 539(20)	−918(14)
C(15)	751(11)	1 306(19)	−1 750(10)
O(1)	3 465(10)	−2 432(19)	3 650(11)
O(2)	4 654(14)	−2 141(24)	3 340(15)
O(3)	4 343(14)	−4 155(24)	3 777(14)
O(4)	4 338(15)	−2 583(24)	4 623(18)
O(W)	7 500	2 500	4 736(21)

Crystal data. $C_{30}H_{28}Cl_2N_4O_8Rh_2{\cdot}H_2O$, $M = 867.31$, orthorhombic, $a = 17.539(11)$, $b = 10.252(7)$, $c = 17.211(12)$ Å, $U = 3\,095(4)$ Å^3, $Z = 4$, $D_c = 1.862$ g cm^{-3}, $F(000) = 1\,736$, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 12.84 cm^{-1}, space group *Pccn* from systematic absences.

Intensity data were collected in the same diffractometer using niobium-filtered Mo-K_α radiation and the θ—2θ scan technique. The intensity of one standard reflection was measured after 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. A total of 2 922 independent reflections was measured (θ 3—25°) of which 1 427, having $I \geqslant 2\sigma(I)$, were considered observed and employed in the analysis. The structure amplitudes were obtained after the usual Lorentz and polarization reduction and the absolute scale was established first by Wilson's method and then by least-squares refinement. No correction for absorption was applied in view of the low absorbance of the sample.

Structure determination and refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares using the SHELX system of computer programs[37] with initially isotropic and then anisotropic thermal parameters for all the non-hydrogen atoms except the oxygen atoms of the perchlorate anion and of the water molecule. The hydrogen atoms (except for those of the water molecule) were placed at their geometrically calculated positions and included in the final structure-factor calculations with isotropic thermal parameters. The final *R* value was 0.063 for the observed reflections only. The atomic scattering factors used, corrected for the anomalous dispersion of Rh and Cl, were taken from ref. 38. The function minimized in the least-squares calculations was $\Sigma w|\Delta F|^2$; unit weights were chosen in the first stages of the refinement, then a weight calculated as $w = K/[\sigma^2(F_o) + gF_o^2]$ with $K = 1.0844$ and $g = 0.003\,56$ in the last cycles of refinement.

Final atomic co-ordinates are given in Table 3. All calculations were performed on the CYBER 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia

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