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Binuclear Dirhodium(I) Complexes with Phenyl(2-pyridyl)amido Ligands. Crystal and Molecular Structure of [{Rh(μ-*N*,*N*′-PhNPy)(nbd)}$_2$]$\cdot$H$_2$O (nbd = 2,5-norbornadiene)

FERNANDO J. LAHOZ, FERNANDO VIGURI, MIGUEL A. CIRIANO, LUIS A. ORO

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009 Saragossa, Spain

CONCEPCION FOCES-FOCES and FELIX H. CANO

Departamento de Rayos-X, Instituto Rocasolano, Consejo Superior de Investigaciones Científicas, Serrano 119, 28006 Madrid, Spain

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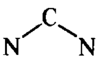
Abstract

The binuclear amidorhodium(I) complexes [{Rh(μ-*N*,*N*′-PhNPyR)(diolefin)}$_2$] and [{Rh(μ-*N*,*N*′-PhNPyR)(CO)$_2$}$_2$] [PhNPyR = phenyl(2-pyridyl)amido, phenyl(4-tertbutyl-2-pyridyl)amido; diolefin = 2,5-norbornadiene, tetrafluorobenzobarrelene] are obtained by reaction of the lithium derivatives LiPhNPyR with the appropriate compound [{RhCl(L$_2$)}$_2$] [L$_2$ = diolefin, (CO)$_2$] and characterized by analytical and spectroscopic methods.

The crystal structure of [{Rh(μ-*N*,*N*′-PhNPy)(nbd)}$_2$]$\cdot$H$_2$O has been solved by X–ray diffraction methods. The $P2_1/n$ monoclinic unit cell has dimensions $a = 20.7787(12)$, $b = 15.4540(7)$, $c = 10.0162(3)$ Å with $\beta = 92.205(4)°$. The final R factor is 0.06 for the 3346 observed reflections. The binuclear unit presents a distorted square-planar coordination around each metal centre with a Rh–Rh separation of 2.959(1) Å. The phenyl(2-pyridyl)amido ligands are bridging the two metallic centres and two 2,5-norbornadiene groups complete the rhodium coordination.

Introduction

Increasing attention is being given to molecules in which two or more rhodium atoms are held in close proximity, because of interest in possible effects derived from the mutual influence of neighbouring metal centres [1–3]. Among those, we have already reported some dirhodium(I) complexes with binucleating ligands containing



bridging units [4–7]. We now report the preparation of binuclear diolefin or carbonyl rhodium(I) complexes with the deprotonated form of 2-(*N*-anilino)-pyridine (PyNPy$^-$) type ligands, and the structure of the compound [{Rh(μ-*N*,*N*′-PhNPy)(nbd)}$_2$]$\cdot$H$_2$O determined by X-ray crystallography. The PhNPy$^-$ ligand has been recently utilized as a bridging ligand by Cotton and coworkers for the formation of bonds between metal atoms [8].

Results and Discussion

Reaction of the compound [{RhCl(diolefin)}$_2$] with a solution of the lithium salt of 2-(*N*-anilino)-pyridine [9] or 2-(*N*-anilino)-4-tertbutylpyridine in diethylether gives straightforward the compounds [{Rh(μ-*N*,*N*′-PhNPy)(diolefin)}$_2$] [diolefin = 2,5-norbornadiene (nbd) (**1**), tetrafluorobenzobarrelene (tfb) (**2**)] or [{Rh(μ-*N*,*N*′-PhNPyBu^t)(diolefin)}$_2$] [diolefin = nbd (**3**), tfb (**4**)] respectively and lithium chloride. Compounds **1**–**4** are isolated as red air-stable crystalline solids in high yields. They are soluble in dichloromethane and toluene, and **3** even in hexane, and behave as non-electrolytes in solution. As expected, a resonance due to the amine proton and ν(N–H) in the 3600–3100 cm^{-1} region are absent in the ^{1}H NMR and in the IR spectra of complexes **1**–**4**. Consequently **1**–**4** contain the nitrogen-donor ligands as amido groups. Amide derivatives of the platinum metals group are scarce and those known are stabilized by ligands having no β-hydrogens [3, 8, 10] such as the compounds above described.

Molecular weight measurements in chloroform solutions of the complexes **1**–**4** suggest a binuclear formulation, although in general the values found are smaller than the calculated ones (see 'Experimental'). The ^{1}H NMR spectra of the compounds **1**–**4** in CDCl$_3$ at 20 °C show the presence of two species in solution, which could give account for the

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low values of their molecular weights. The relative proportions are 90:10 for **1**, 95:5 for **2**, 65:35 for **3** and 85:15 for **4**; they are invariable even if the temperature is lowered at −40 °C and therefore both species do not interconvert. The ^{1}H NMR spectra of the main species (given in Table I) are in accordance with a rigid binuclear structure having an element of symmetry that makes magnetically equivalent the chemically equivalent protons of both $PhNPy^-$ or $PhNPyBu^{t-}$ ligands. This element of symmetry also relates the olefinic and tertiary protons of one diolefin ligand to those of the other in sets of two, but inside of each diolefin all of them are magnetically inequivalent giving rise to six distinct resonances. Two hypothetical structures in accord with such ^{1}H NMR spectrum are **A** (symmetry C_2) and **B** (symmetry C_i) (Fig. 1); the rigidness of each one being imposed by the bulkiness of the phenyl ring.

In order to ascertain for the structure of the complexes in the solid state, suitable crystals for X-ray diffraction studies of compound **1** were grown in acetone–water (see below).

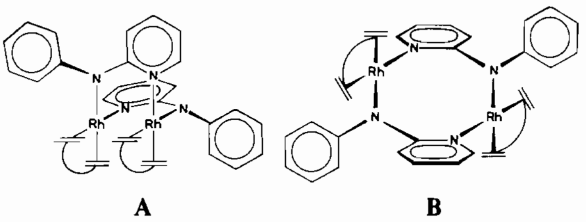


Fig. 1. Hypothetical structures for the binuclear phenyl(2-pyridyl)amido diolefin rhodium complexes.

The minoritaire species could be a head-to-head isomer of **A** (Fig. 1) or, alternatively, could be formed by reaction of the main species with chloroform. Thus complex **3** is recovered after reflux in toluene for 1 h whilst a similar reflux in chloroform gives a mixture of a brown and a yellow solid containing chloride. We suspect that this yellow compound could be mononuclear and would account for the low molecular weights observed in chloroform solution.

Bubbling of carbon monoxide through a solution of **3** in hexane produces a black insoluble residue and a mixture of carbonylrhodium complexes in solution. However, reaction of $[\{RhCl(CO)_2\}_2]$ with LiPhNPy or $LiPhNPyBu^t$ in diethylether yields the compounds $[\{Rh(\mu\text{-}N,N'\text{-}PhNPy)(CO)_2\}_2]$ (**5**) or $[\{Rh(\mu\text{-}N,N'\text{-}PhNPyBu^t)(CO)_2\}_2]$ (**6**) as red solids that decompose slowly at room temperature. Although we have not obtained fully satisfactory elemental analyses for **5** and **6** their IR spectra in pentane show a pattern of four terminal ν(CO) bands characteristic of binuclear rhodium(I) complexes having a nearly face to face disposition of the square-planar environments of the rhodium atoms in which the carbonyl ligands are in a *cis*-$Rh(CO)_2$ arrangement such as that found in $[\{Rh(\mu\text{-}Onapy)(CO)_2\}_2]$ [5].

Finally the binuclear complexes **1** and **3** are active catalyst precursors, in the presence of potassium hydroxide, for the transfer of hydrogen in refluxing isopropanol to cyclohexene or acetophenone [11, 12]. The results show that complex **3** reduces acetophenone more rapidly than cyclohexene (78% for acetophenone and 55% for cyclohexene after one hour) whilst a reverse situation is found for complex **1** (22% for acetophenone and 68% for cyclohexene after one hour).

TABLE I. ^{1}H NMR Spectra for Ligands and Complexes **1**–**4**[a]

PhNHPy	8.21(ddd, 1 H, ^3J 5.0 ^4J 1.9 ^5J 0.9, H-6) 7.49(ddd, 1 H, ^3J 8.4 ^3J 7.2 ^4J 1.9, H-4) 7.34(m, 4 H, C_6H_5) 7.05(m, 1 H, C_6H_5) 6.9(br, 1 H, NH) 6.90(ddd, 1 H, ^3J 8.4 ^4J0.9 ^5J 0.9, H-3) 6.73(ddd, 1 H, ^3J 7.2 ^3J 5.0 ^4J 0.9, H-5).
$PhNHPyBu^t$	8.13(dd, 1 H, ^3J 5.5 ^5J 0.7, H-6) 7.35(m, 4 H, C_6H_5) 7.0(m, 1 H, C_6H_5) 6.89(dd, 1 H, ^4J 1.7 ^5J 0.7, H-3) 6.77(dd, ^3J 5.5 ^4J 1.7, H-5) 6.7(br, 1 H, NH) 1.34(s, 9 H, Bu^t).
1	8.35(d, 2 H, H-6) 7.36(m, 4 H, C_6H_5) 7.07(m, 6H, C_6H_5) 6.62(ddd, 2 H, H-4) 5.93(ddd, 2 H, H-5) 5.62(d, 2H, H-3) 4.18(m, 4 H, nbd) 4.06(m, 2 H, nbd) 3.78(m, 2 H, nbd) 3.36(m, 2 H, =CH nbd) 3.27(m, 2 H, =CH nbd) 1.22(s, 4 H, CH_2 nbd).
2	8.42(d, 2 H, H-6) 7.35(m, 4 H, C_6H_5) 7.08(m, 6 H, C_6H_5) 6.73(ddd, 2 H, H-4) 6.06(m, 4 H, H-5 and tfb) 5.68(d, 2 H, H-3) 5.62(m, 2 H, tfb) 3.97(t, 2 H, =CH tfb) 3.79(t, 2 H, =CH tfb) 3.17(t, 2 H, =CH tfb) 3.09(t, 2 H, =CH tfb).
3	8.18(d, 2 H, H-6) 7.33(m, 4 H, C_6H_5) 7.09(m, 6 H, C_6H_5) 5.91(dd, 2 H, H-5) 5.59(d, 2 H, H-3) 4.16(m, 4 H, nbd) 4.03(m, 2 H, nbd) 3.77(m, 2 H, nbd) 3.38(m, 2 H, =CH nbd) 3.28(m, 2 H, =CH nbd) 1.25(s, 4 H, CH_2 nbd) 0.90(s, 18 H, Bu^t).
4	8.34(d, 2 H, H-6) 7.32(m, 4 H, C_6H_5) 7.05(m, 6 H, C_6H_5) 6.05(dd, 2 H, H-5) 6.0(m, 2 H, tfb) 5.65(dd, 2 H, H-3) 5.61(m, 2 H, tfb) 3.96(t, 2 H, =CH tfb) 3.75(t, 2 H, =CH tfb) 3.18(m, 2 H, =CH tfb) 3.10(m, 2 H, =CH tfb) 0.93(s, 18 H, Bu^t).

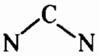
[a] in $CDCl_3$ at 20 °C; chemical shifts in δ(ppm). Abbreviations: dd = doublet of doublets, ddd = double doublet of doublets, m = multiplet; br = broad band. Coupling constants in Hz.

Description of the Structure of [{Rh(μ-PhNPy)(nbd)}$_2$]·H$_2$O

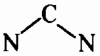
The crystal structure consists of binuclear molecules [{Rh(μ-PhNPy)(nbd)}$_2$] and water of crystallization. A view of the molecular structure with the atomic numbering scheme is given in Fig. 2. Selected geometrical parameters are given in Table II. The complex presents a pseudo two-fold axis through the mid-point of Rh(1)•••Rh(2) relating to two phenyl-(2-pyridyl)amido and 2,5-norbornadiene ligands. This binuclear complex shows two exo-bidentate phenyl-(2-pyridyl)amido ligands bridging the two metals through the nitrogen atoms; the coordination around each rhodium atom is completed by a norbornadiene molecule interacting through the olefinic bonds. Each rhodium atom appears in a distorted square-planar environment involving the two types of nitrogen atoms and the midpoints [C(224), C(227) and C(334), C(331)] of the olefinic bonds.

The values of the torsion angles around the Rh(1)•••Rh(2) line (see Table II) show the relative twist of the coordination planes, that of the two phenyl(2-pyridyl)amido ligands and the relative disposition of the two 2,5-norbornadiene ligands. For each metal atom the four coordinating points are not planar and their least-squares planes make an angle of 48.2(3)°.

The Rh•••Rh separation, 2.959(1) Å, and the deviation of the rhodium atoms from the square-planar coordination towards the other metal atom, suggest some metal–metal interaction [4, 6]. A similar situation has been recently observed in related rhodium(I) complexes with binucleating ligands containing


$\mathrm{N{-}C{-}N}$

bridging units (see Table III). It is interesting to point out the relative flexibility of the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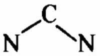
binucleating ligands, as seen in the range of intermetallic separations rhodium–rhodium in this complex, 2.959(1) Å *versus* ruthenium–ruthenium in [Ru$_2$Cl(μ-PhNPy)$_4$], 2.275(3) Å [8b]; or rhodium–rhodium distances of 3.207(3) and 2.686(2) Å in the 7-azaindolato (az) complexes [Rh$_2$(μ-az)$_2$(nbd)$_2$] and [Rh$_4$(μ-Cl)$_2$(μ-az)$_2$(μ-CO)$_2$(CO)$_2$(nbd)$_2$] [7]). Table III collects a comparison of structural parameters for dirhodium complexes containing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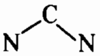
bridging units; it shows that the Rh–N distances and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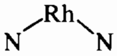
or

$\mathrm{N{-}Rh{-}N}$,

angles of the complex described in this paper compare well with related binuclear rhodium(I) complexes [4–7].

The Rh–N–C–N–Rh rings are not planar (see Table II) and their puckering is quite similar, both in a twist fashion [13]. The least squares planes through these rings make an angle of 90.9(2)°. The Rh distances to the midpoints of the olefinic bonds present some asymmetry (2.014(10), 2.003(9) *versus* 1.992(10), 1.903(9) Å) [2–4], and the corresponding coordination planes make an angle of 60.1(4)° one with each other and each one with the respective diolefin plane 90.6(5) and 88.5(5)°, corresponding to a perpendicular bonding.

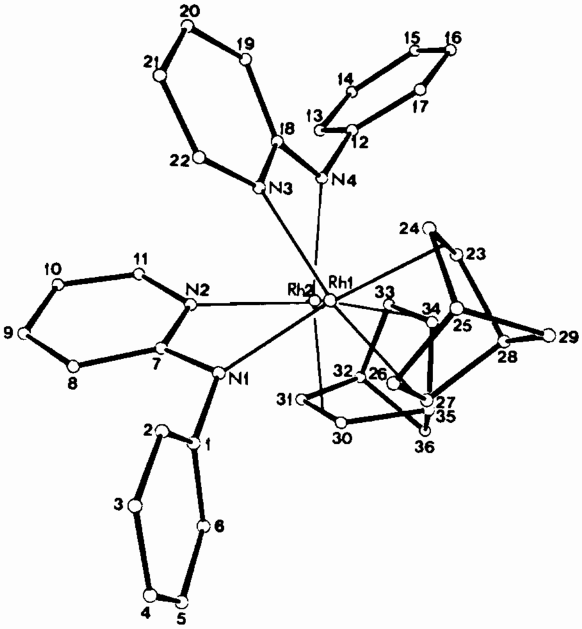


Fig. 2. A view of the molecular structure of complex **1** with the atomic numbering scheme. The symbols for the carbon atoms are omitted for clarity.

Experimental

All reactions were carried out under a nitrogen atmosphere using Schlenck techniques. Solvents were dried and distilled under nitrogen immediately prior to use. Elemental analyses were carried out with a Perkin-Elmer 240B microanalyzer. IR spectra (range 4000–200 cm^{-1}) were recorded on a Perkin-Elmer 783 spectrometer using Nujol mulls between polyethylene sheets or pentane solutions in NaCl cells. Molecular weights were determined with a Knauer osmometer using chloroform solutions. ^{1}H NMR

TABLE II. Selected Bond Distances (Å) and Bond Angles (°)

(a) Bond distances			
Rh(1)–Rh(2)	2.959(1)		
Rh(1)–N(1)	2.073(9)	Rh(2)–N(2)	2.111(9)
Rh(1)–N(3)	2.016(10)	Rh(2)–N(4)	2.094(11)
Rh(1)–C(23)	2.100(13)	Rh(2)–C(30)	2.131(14)
Rh(1)–C(24)	2.109(12)	Rh(2)–C(31)	2.135(14)
Rh(1)–C(26)	2.123(13)	Rh(2)–C(32)	2.137(14)
Rh(1)–C(27)	2.124(14)	Rh(2)–C(34)	2.104(14)
Rh(1)–C(224)[a]	1.983(9)	Rh(2)–C(334)[a]	1.992(10)
Rh(1)–C(227)[a]	2.003(9)	Rh(2)–C(331)[a]	2.014(10)
N(1)–C(1)	1.432(14)	N(4)–C(12)	1.400(15)
N(1)–C(7)	1.363(14)	N(4)–C(18)	1.360(15)
N(2)–C(7)	1.381(13)	N(3)–C(18)	1.355(14)
N(2)–C(11)	1.348(15)	N(3)–C(22)	1.376(15)
C(23)–C(24)	1.411(19)	C(30)–C(31)	1.406(20)
C(26)–C(27)	1.408(21)	C(33)–C(34)	1.454(20)
(b) Bond angles			
N(1)–Rh(1)–N(3)	89.8(4)	N(2)–Rh(2)–N(4)	91.4(4)
N(1)–Rh(1)–C(224)[a]	171.7(4)	N(2)–Rh(2)–C(334)[a]	162.5(4)
N(1)–Rh(1)–C(227)[a]	101.0(4)	N(2)–Rh(2)–C(331)[a]	96.7(4)
N(3)–Rh(1)–C(224)[a]	97.3(4)	N(4)–Rh(2)–C(334)[a]	99.7(4)
N(3)–Rh(1)–C(227)[a]	164.2(4)	N(4)–Rh(2)–C(331)[a]	170.8(4)
C(224)–Rh(1)–C(227)[a]	71.2(4)	C(331)–Rh(2)–C(334)[a]	71.5(4)
C(1)–N(1)–Rh(1)	120.2(7)	C(12)–N(4)–Rh(2)	119.6(8)
C(7)–N(1)–Rh(1)	122.7(7)	C(18)–N(4)–Rh(2)	120.0(8)
C(1)–N(1)–C(7)	115.8(9)	C(12)–N(4)–C(18)	118.3(10)
C(7)–N(2)–Rh(2)	123.6(7)	C(18)–N(3)–Rh(1)	125.2(8)
C(11)–N(2)–Rh(2)	118.0(7)	C(22)–N(3)–Rh(1)	116.6(8)
N(1)–C(7)–N(2)	116.1(9)	N(3)–C(18)–N(4)	116.7(10)
(c) Torsion angles			
N(1)–Rh(1)–Rh(2)–N(2)	32.0(3)	C(224)–Rh(1)–Rh(2)–N(2)	154.1(4)
N(1)–Rh(1)–Rh(2)–N(4)	126.2(4)	C(224)–Rh(1)–Rh(2)–N(4)	59.9(4)
N(1)–Rh(1)–Rh(2)–C(331)	61.0(4)	C(224)–Rh(1)–Rh(2)–C(331)	112.9(4)
N(1)–Rh(1)–Rh(2)–C(334)	139.2(4)	C(224)–Rh(1)–Rh(2)–C(334)	34.7(4)
N(3)–Rh(1)–Rh(2)–N(2)	61.2(4)	C(227)–Rh(1)–Rh(2)–N(2)	127.8(4)
N(3)–Rh(1)–Rh(2)–N(4)	33.0(4)	C(227)–Rh(1)–Rh(2)–N(4)	137.9(4)
N(3)–Rh(1)–Rh(2)–C(331)	154.2(4)	C(227)–Rh(1)–Rh(2)–C(331)	34.9(4)
N(3)–Rh(1)–Rh(2)–C(334)	127.7(4)	C(227)–Rh(1)–Rh(2)–C(334)	43.3(5)
Rh(2)–Rh(1)–N(1)–C(7)	44.4(8)	Rh(1)–Rh(2)–N(4)–C(8)	44.4(8)
Rh(1)–N(1)–C(7)–N(2)	32.0(12)	Rh(2)–N(4)–C(18)–N(3)	30.9(13)
N(1)–C(7)–N(2)–Rh(2)	16.2(13)	N(4)–C(18)–N(3)–Rh(1)	18.6(14)
C(7)–N(2)–Rh(2)–Rh(1)	35.8(8)	C(18)–N(3)–Rh(1)–Rh(2)	38.7(9)
C(2)–C(1)–N(1)–C(7)	99.6(15)	C(13)–C(12)–N(4)–C(18)	104.6(15)
C(1)–N(1)–C(7)–N(2)	161.5(9)	C(12)–N(4)–C(18)–N(3)	165.7(10)

[a] C(224), C(227), C(331) and C(334) are the midpoints of the olefinic bonds.

spectra were recorded on a Varian XL-200 spectrometer operating at 200.057 MHz. Tetramethylsilane was used as standard.

The complexes $[\{RhCl(diolefin)\}_2]$ (diolefin = nbd [14], tfb [15]) were prepared according to literature methods. 2-(N-anilino)pyridine was prepared as described by Seidl *et al.* [16].

Preparation of 2-(N-anilino)-4-tertbutylpyridine

Phenylisocyanate (12.0 ml, 0.11 mol) was added to a solution of 4-tertbutylpyridine-*N*-oxide (7.8 g, 0.05 mol) in dimethylformamide (20 ml) at room temperature with evolution of carbon dioxide. The mixture was warmed at 110 °C for 8 h and then the solvent was pumped off at 100 °C. Sublimation of the

TABLE III. Comparison of Structural Parameters for Rhodium(I) Complexes with Binucleating Ligands Containing $N\overset{C}{\wedge}N$ Bridging Units

Complex	Rh···Rh (Å)	ΔRh (Å)[a]	$N\overset{C}{\wedge}N$ (°)	$N\overset{Rh}{\wedge}N$ (°)	Rh–N (Å)	Reference
$[Rh_2(\mu\text{-PhNPy})_2(nbd)_2]$	2.959(1)	0.149(1), 0.132(1)	116.1(9), 116.7(10)	89.8(4), 91.4(4)	2.073(9)–2.131(14)	This work
$[Rh_2(\mu\text{-napy})_2(nbd)_2]^{2+}$	2.916(3)	0.19(1)	116(1)	87.9(5)	2.12(1)–2.15(1)	4
$[Rh_2(\mu\text{-Onapy})_2(CO)_4]$	2.880(2)	–	118.3(9), 119.7(9)	87.2(5), 87.5(5)	2.098(9)–2.136(10)	5
$[Rh_2(\mu\text{-CPh(NPh)}_2(tfb)_2]$	2.982(3)	0.171(2), 0.172(2)	118.1(5), 120.4(5)	89.4(2), 90.8(2)	2.086(6)–2.138(4)	6
$[Rh_2(\mu\text{-az})_2(nbd)_2]$	3.207(3)	0.158(2)	125(1)	90.3(3)	2.092(7)–2.111(8)	7

[a] ΔRh: Deviation from the square coordination plane towards the other metal.

residue (0.01 torr, 110 °C) and recrystallization of the sublimate from toluene gave the compound of the title as white crystals. Yield: 3.26 g; melting point (m.p.) 134 °C. *Anal.* Found: C, 79.4; H, 7.9; N, 12.7. Calc. for $C_{15}H_{18}N_2$: C, 79.6; H, 8.0; N, 12.4%.

Preparation of the Complexes [{Rh(μ-N,N′-L)(diolefin)}₂] (1–4)

A solution of 2-(*N*-anilino)pyridine (102 mg, 0.6 mmol) or 2-(*N*-anilino)-4-tertbutylpyridine (136 mg, 0.6 mmol) in diethylether (10 ml) was reacted with a solution of butyllithium (1.4 mol l^{-1} in hexane, 0.43 ml, 0.6 mmol) for 10 min to give a pale-yellow solution. The appropriate compound [{RhCl(diolefin)}$_2$] (diolefin = nbd, tfb) (0.3 mmol) was then added and the mixture was stirred for 30 min to give a red suspension. The solvent was removed under vacuum and the residue was washed with a mixture of acetone:water 1:1 (5 ml) to yield compounds **1**–**4** as red solids which were filtered and vacuum-dried.

1. Yield: 92%. *Anal.* Found: C, 58.6; H, 4.9; N, 7.72; $M = 670$ (in $CHCl_3$). Calc. for $C_{36}H_{34}N_4Rh_2$: C, 59.35; H, 4.70; N, 7.69%; $M = 728$.

2. Yield: 98%. *Anal.* Found: C, 54.9; H, 3.1; N, 5.27; $M = 795$ (in $CDCl_3$). Calc. for $C_{46}H_{30}F_8N_4Rh_2$: C, 55.4; H, 3.03; N, 5.62%; $M = 997$.

3. Yield: 94%. *Anal.* Found: C, 62.4; H, 5.8; N, 6.51; $M = 646$. Calc. for $C_{44}H_{50}N_4Rh_2$: C, 62.9; H, 6.00; N, 6.66%; $M = 840$.

4. Yield: 85%. *Anal.* Found: C, 57.8; H, 4.7; N, 5.00; $M = 701$. Calc. for $C_{54}H_{46}F_8N_4$: C, 58.5; H, 4.2; N, 5.05%; $M = 1108$.

Preparation of [{Rh(μ-N,N′-L)(CO)₂}₂] (5, 6)

Reaction of the compound [{RhCl(CO)$_2$}$_2$] (78 mg, 0.2 mmol) with a solution of LiPhNPy or LiPhNPyBu^t (0.4 mmol) in diethylether (10 ml) (prepared as described above) for 15 min gave a dark-red solution. After removal of the solvent under vacuum, the residue was extracted with hexane. Evaporation of the extracts to *ca.* 1 ml and cooling overnight in the freezer gave the compounds as red solids in 30 and 40% yield respectively.

5. *Anal.* Found: C, 45.8; H, 3.1; N, 7.5. Calc. for $C_{26}H_{18}N_4O_4Rh_2$: C, 47.6; H, 2.8; N, 8.5%; ν(CO): 2080vs, 2055s, 2010vs, 2005m cm^{-1} (pentane); 2080s, 2050s, 2030s, 2010s, 1995s, 1985s cm^{-1} (Nujol).

6. *Anal.* Found: C, 51.1; H, 5.1; N, 6.2. Calc. for $C_{34}H_{34}N_4O_4Rh_2$: C, 53.15; H, 4.7; N, 7.3%. ν(CO): 2075vs, 2050s, 2005vs, 1995m cm^{-1} (pentane); 2075s, 2050s, 2005s, 1990s cm^{-1} (Nujol).

Catalytic Activity

The transfer hydrogenation reactions were carried out using equipments and conditions previously reported [11].

TABLE IV. Crystal Analysis Parameters

Crystal data	
Formula	$[\{Rh(\mu\text{-}N,N'\text{-}PhNPy)(nbd)\}_2]\cdot H_2O$
Crystal habit	prismatic plate, hexagonal basis; red
Crystal size (mm)	0.07 × 0.23 × 0.33
Symmetry	monoclinic, $P2_1/n$
Unit cell determination	least-squares fit from 94 reflections ($\theta < 45°$)
Unit cell dimensions	a = 20.7787(12), b = 15.4540(7), c = 10.0162(3) Å, α = 90, β = 92.205(4), γ = 90°
Packing: V (Å^3), Z	3214.0(3), 4
D (g cm^{-3}), M, F(000)	1.543, 746.52, 1512
μ (cm^{-1})	87.56
Experimental data	
Technique	four circle diffractometer Philips PW 1100 bisecting geometry graphite oriented monochromator: Cu Kα radiation $\omega/2\theta$ scans, 1.5 scan width detector apertures 1 × 1, up to θ_{max} = 65° 1 min/reflection
Number of reflections	
Independent	5471
Observed	3346 (4 $\sigma(I)$ criterion) 2 reflections every 90 minutes, no variation
Absorption correction	0.739–1.514
Solution and refinement	
Solution	Patterson
Refinement	least-squares on F_{obs} with 1 block
Parameters	
number of variables	388
degrees of freedom	2958
ratio of freedom	8.6
H atoms	difference synthesis, but those of the water molecule
Final shift/error	0.04
Weighting scheme	empirical as to give no trends in $\langle w\Delta^2F\rangle$, vs. $\langle\lvert F_{obs}\rvert\rangle$ or $\langle\sin\theta/\lambda\rangle$
Maximum thermal value	U_{22}(C5) = 0.27(4) Å^2
Final ΔF peaks	1.5 e Å^{-3}
Final R and R_w	0.060, 0.075
Computer and programs	Vax 11/750, DIFABS [17], XRAY76 [18]
Scattering factors	International Tables for X-ray Crystallography [19]

X-ray Analysis

Crystal analysis parameters are given in Table IV. One crystallization water molecule per dinuclear unit was found in the structure. The hydrogen atoms were found in a difference synthesis and kept fixed during the refinement. The final atomic coordinates are given in Table V.

TABLE V. Final Atomic Coordinates

Atom	x/a	y/b	z/c
Rh(1)	0.18273(4)	0.21272(5)	0.02801(8)
Rh(2)	0.26259(4)	0.34482(5)	0.16985(8)
O(W)	0.0128(7)	0.0277(12)	0.8496(26)
N(1)	0.1316(4)	0.3258(6)	−0.0103(9)
N(2)	0.1684(4)	0.3939(5)	0.1855(9)
N(3)	0.1502(5)	0.2120(6)	0.2246(10)
N(4)	0.2479(5)	0.2544(7)	0.3213(11)
C(1)	0.0939(6)	0.3352(8)	−0.1320(12)
C(2)	0.0414(9)	0.2871(11)	−0.1566(23)
C(3)	0.0059(12)	0.2927(17)	−0.2809(41)
C(4)	0.0280(12)	0.3456(24)	−0.3770(23)
C(5)	0.0795(14)	0.3929(27)	−0.3537(18)
C(6)	0.1149(7)	0.3892(16)	−0.2287(15)
C(7)	0.1209(5)	0.3858(7)	0.0861(10)
C(8)	0.0651(7)	0.4383(9)	0.0886(14)
C(9)	0.0567(7)	0.4920(9)	0.1976(14)
C(10)	0.1012(7)	0.4941(8)	0.3026(14)
C(11)	0.1564(6)	0.4454(8)	0.2903(12)
C(12)	0.2937(6)	0.2461(8)	0.4269(11)
C(13)	0.3109(9)	0.3156(10)	0.5112(14)
C(14)	0.3577(11)	0.3095(11)	0.6074(15)
C(15)	0.3926(8)	0.2331(14)	0.6254(15)
C(16)	0.3773(9)	0.1640(12)	0.5440(19)
C(17)	0.3278(7)	0.1714(9)	0.4467(13)
C(18)	0.1883(5)	0.2203(7)	0.3367(11)
C(19)	0.1647(6)	0.1936(8)	0.4617(11)
C(20)	0.1017(7)	0.1698(10)	0.4717(12)
C(21)	0.0610(7)	0.1702(9)	0.3593(15)
C(22)	0.0865(5)	0.1911(8)	0.2395(12)
C(23)	0.2587(6)	0.1232(9)	0.0443(12)
C(24)	0.1998(7)	0.0782(8)	0.0294(13)
C(25)	0.1899(8)	0.0646(8)	−0.1218(14)
C(26)	0.1768(7)	0.1576(10)	−0.1662(12)
C(27)	0.2363(7)	0.2004(9)	−0.1474(13)
C(28)	0.2833(6)	0.1337(9)	−0.0951(13)
C(29)	0.2586(8)	0.0509(11)	−0.1658(15)
C(30)	0.2879(6)	0.3995(10)	−0.0162(14)
C(31)	0.2956(6)	0.4626(9)	0.0844(14)
C(32)	0.3664(6)	0.4545(9)	0.1359(16)
C(33)	0.3625(7)	0.3705(10)	0.2095(14)
C(34)	0.3533(6)	0.3026(9)	0.1100(15)
C(35)	0.3534(6)	0.3544(11)	−0.0233(13)
C(36)	0.3993(7)	0.4293(12)	0.0110(16)

Supplementary Material

Thermal parameters, hydrogen coordinates and structural factors can be obtained from the Editor-in-Chief in Padua on request.

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