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Syntheses and structures of dinuclear rhodium(I) complexes and 1-D zigzag-chain rhodium(I) co-ordination polymers bridged by rod-like bidentate nitrogen ligands†

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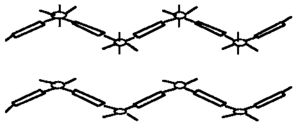
Novel dinuclear rhodium(I) complexes, $[Rh_2(2\text{-bpbd})_2(cod)_2]X_2$ (X = BF_4 **1a**, PF_6 **1b** or ClO_4 **1c**; cod = cycloocta-1,5-diene) and 1-D rhodium(I) co-ordination polymers with the linkage of square-planar rhodium(I) centers, $\{[Rh(4\text{-bpbd})(cod)]X\}_n$ (X = BF_4 **2a**, PF_6 **2b** or ClO_4 **2c**) and $\{[Rh(4\text{-bpe})(cod)]X\}_n$ (X = BF_4 **3a**, PF_6 **3b** or ClO_4 **3c**), were systematically synthesized using 1,4-bis(2-pyridyl)butadiyne (2-bpbd), 1,4-bis(4-pyridyl)butadiyne (4-bpbd) and *trans*-1,2-bis(4-pyridyl)ethylene (4-bpe). The structures of **1a**, **2a**, **2b** and **3a** were crystallographically characterized. In **1a** each Rh atom is bridged by two N atoms of 2-bpbd to afford a unique dinuclear structure with an 18-membered $Rh_2N_4C_{12}$ framework. In **2a**, **2b** and **3a**, each Rh atom is bonded to two N atoms of 4-bpbd (**2a** and **2b**) or 4-bpe (**3a**) and two C=C bonds of cod in a square-planar geometry. The square-planar centers are in turn linked by 4-bpbd or 4-bpe ligands to form a 1-D zigzag-chain structure. The zigzag chains are located in parallel 9.6, 9.9 and 10.7 Å apart in **2a**, **2b** and **3a**, respectively, and no effective intermolecular interactions were found.

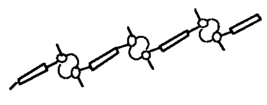
Introduction

Crystal engineering and the design of solid-state architectures have recently become quite interesting and exciting areas of research.[1] Assembling extended-structure compounds by selecting the chemical structures of organic ligands and the co-ordination geometry of metals can yield numerous co-ordination polymers with various dimensionalities, sizes, cavities and shapes. Self-assembly is also the most efficient approach toward the design of 1-D, 2-D, and 3-D organic/inorganic hybrid materials of potential utility in fields such as catalysis,[2] nonlinear optics,[3] molecular magnetic materials,[4] electrical conductivity,[5] and molecular recognition.[6] Many researchers have proposed strategies for the design of new crystal phases, assembled from suitable metal centers and organic molecules of different nature and size. Most of the simplest linking ligands are bifunctional rod-like ligands such as 4,4′-bipyridine (4,4′-bpy) and related species, which are chosen in order to construct linear building blocks. A number of 1-D co-ordination polymers with 4,4′-bpy have been characterized together with the 2-D[7] and 3-D[6a,8] co-ordination polymers with 4,4′-bpy in the shape of layers, networks, channels and cavities. For instance, 1-D zigzag-chain structures (a) have been found in $[Cu(tta)(4,4'\text{-bpy})]_n$ (tta = 2-thienoyltrifluoroacetone),[9a] $[Cu(4,4'\text{-bpy})(MeCN)_2]_n$,[9b] $\{[Cu(4,4'\text{-bpy})(dmp)]BF_4\}_n$,[9c] $\{[Mn(4,4'\text{-bpy})\{N(SiMe_3)_2\}_2]\cdot thf\}_n$,[9d] $[Ni(4,4'\text{-bpy})(EtXA)_2]_n$ (EtXA = *O*-ethyl dithiocarbonate),[9e] $[Cu(2,2'\text{-bpy})(4,4'\text{-bpy})(ClO_4)_2]_n$,[9f] $[Zn\{(C_2H_5O)_2S_2P\}_2(4,4'\text{-bpy})]_n$[9g] and $[Zn(SPh)_2(4,4'\text{-bpy})_2]_n$.[9h] The 1-D straight-chain structures (b) have also been obtained for $[Mn(4,4'\text{-bpy})_2(NCS)_2(H_2O)_2]_n$,[5a] $[Co(Hdmg)_2(4,4'\text{-bpy})]_n$,[10b] $[Co(H_2O)_3(4,4'\text{-bpy})_2(SO_4)]_n$,[10c] $[Co(DMSO)_2(4,4'\text{-bpy})_2Cl_2]_n$,[10c] $[Ni(S_2COBu)_2(4,4'\text{-bpy})\cdot 2CCl_4]_n$,[10d] $\{[Cu(4,4'\text{-bpy})(C_5H_4F_3O_2)]\}$,[10e] $[Cd(4,4'\text{-bpy})(ipxa)_2]_n$ (ipxa = *O*-isopropyl dithiocarbonate)[10f] and $[Me_3Sn(SO_2Me)_2(4,4'\text{-bpy})]_n$.[10g] The 1-D stair-step chain structures (c) have been observed in $[Cu_2(NO_3)_2(PPh_3)_2(4,4'\text{-bpy})\cdot 2thf]_n$,[11a] $[Cu_2(\mu\text{-}Cl)_2(PPh_3)_2(4,4'\text{-bpy})]_n$[11b] and $\{[Cu_2(pt)_2(4,4'\text{-bpy})(NO_3)_2(H_2O)_2]\cdot 4H_2O\}_n$ (pt = 3-pyridin-2-yl-1,2,4-triazolato).[11c] On the base of the above, it seems that the shapes of the 1-D co-ordination polymers are primarily due to the co-ordination geometry of each transition metal. The ions Cu^I, Mn^{II} and Zn^{II} normally form the 1-D zigzag-chain or stair-step structure with the linkage of pseudo-tetrahedral metal centers; Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Cd^{II} afford 1-D zigzag- or straight-chain structures with the linkage of pseudo-octahedral metal centers. However, 1-D co-ordination polymers with linkage of square-planar metal centers by rod-like ligands have rarely been observed.



(a) 1-D zigzag-chain structures

(b) 1-D straight-chain structures



(c) 1-D stair-step structures

Incidentally, it is well known that Rh^I and Rh^{III} generally prefer square-planar and octahedral geometries, respectively, and that rhodium complexes can easily form organometallic compounds. A variety of polynuclear and cluster compounds of Rh have been studied with regard to their metal–metal interactions, specific structures and reactivity.[12] It is expected that its co-ordination polymers would produce interesting structures and properties, not found in polynuclear and cluster compounds. However, there have been few investigative reports of such polymers, and their structures and prop-

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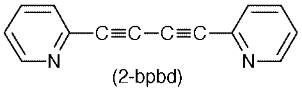
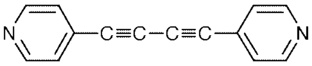
† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4357/

erties are not very obvious. The aim of this study is to illustrate various possibilities regarding the construction of rhodium(I) co-ordination polymers. We attempted here to prepare these using three rod-like ligands, 1,4-bis(2-pyridyl)butadiyne (2-bpbd), 1,4-bis(4-pyridyl)butadiyne (4-bpbd) and *trans*-1,2-bis(4-pyridyl)ethylene (4-bpe). Dinuclear rhodium(I) complexes $[Rh_2(2\text{-bpbd})_2(cod)_2]X_2$ (cod = cycloocta-1,5-diene; X = counter anion) and 1-D rhodium(I) co-ordination polymers $\{[Rh(4\text{-bpbd})(cod)]X\}_n$ and $\{[Rh(4\text{-bpe})(cod)]X\}_n$ with the linkage of square-planar rhodium(I) centers were produced, and their structures crystallographically characterized.


(2-bpbd)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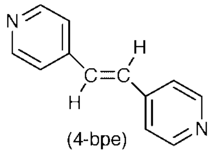
(4-bpe)

Experimental

General procedures

All operations were carried out using the usual Schlenk techniques under an argon atmosphere. The compounds $RhCl_3{\cdot}3H_2O$ and cycloocta-1,5-diene were available from Johnson & Matthey and Tokyo Kasei Chemicals, respectively, and used without further purification. 1,4-Bis(2-pyridyl)butadiyne,[13] 1,4-bis(4-pyridyl)butadiyne[14] and $[Rh(cod)_2]X$ ($X = BF_4$, PF_6 or ClO_4)[15] were prepared according to literature methods. *trans*-1,2-Bis(4-pyridyl)ethylene was purchased from Aldrich and used without further purification. All organic solvents were dried by general methods and distilled before use. Infrared spectra were recorded with a JASCO 8000 spectrometer.

Preparation of dinuclear rhodium(I) complexes and co-ordination polymers

(a) $[Rh_2(2\text{-bpbd})_2(cod)_2][BF_4]_2{\cdot}2Me_2CO$ 1a. Acetone solutions (5 ml each) of $[Rh(cod)_2]BF_4$ (61.5 mg, 0.15 mmol) and 2-bpbd (33.0 mg, 0.15 mmol) were individually prepared in Schlenk tubes under Ar. A 3 ml sample of each solution was layered in a 5 mm diameter glass tube, after which the tube was sealed. The reaction solution was allowed to stand at −30 °C for 3 d and yellow crystals of **1a** were collected. Yield 66 mg (70%). Calc. for $C_{22}H_{20}BF_4N_2Rh{\cdot}2C_3H_6O$: C, 53.60; H, 4.68; N, 5.00. Found: C, 53.86; H, 4.73; N, 5.00%. IR (KBr, cm^{-1}): 1541, 1458 and 1084.

(b) $[Rh(2\text{-bpbd})_2(cod)_2][PF_6]_2$ 1b and $[Rh(2\text{-bpbd})_2(cod)_2][ClO_4]_2$ 1c. Yellow crystals of complexes **1b** and **1c** were prepared in the same manner as for **1a**, using $[Rh(cod)_2]PF_6$ (69.0 mg, 0.15 mmol) and $[Rh(cod)_2]ClO_4$ (63.0 mg, 0.15 mmol), respectively. **1b**: Yield 52 mg (51%). Calc. for $C_{22}H_{20}F_6N_2PRh$: C, 47.16; H, 3.60; N, 5.00. Found: C, 47.36; H, 3.76; N, 4.92%. IR (KBr, cm^{-1}): 1589, 1468, 1429 and 875. **1c**: Yield 53 mg (52%). Calc. for $C_{22}H_{20}ClN_2O_4Rh$: C, 51.33; H, 3.92; N, 5.44. Found: C, 50.73; H, 3.01; N, 4.87%. IR (KBr, cm^{-1}): 1587, 1464, 1427 and 1105.

(c) $\{[Rh(4\text{-bpbd})(cod)]BF_4{\cdot}2Me_2CO\}_n$ 2a. Acetone solutions (5 ml each) of $[Rh(cod)_2]BF_4$ (61.5 mg, 0.15 mmol) and 4-bpbd (33.0 mg, 0.15 mmol) were prepared in Schlenk tubes under Ar. A 3 ml sample of each solution was layered in a 5 mm diameter glass tube, after which the tube was sealed. The solution was allowed to stand at −30 °C for 3 d and yellow crystals of **2a** were collected. Yield 66 mg (70%). Calc. for $C_{22}H_{20}N_2BF_4Rh{\cdot}2C_3H_6O$: C, 54.39; H, 5.22; N, 4.53. Found: C, 53.86; H, 4.73; N, 5.00. IR (KBr, cm^{-1}): 1603, 1487, 1420 and 1080.

(d) $\{[Rh(4\text{-bpbd})(cod)]PF_6{\cdot}2Me_2CO\}_n$ 2b and $\{[Rh(4\text{-bpbd})(cod)]ClO_4\}_n$ 2c. Yellow crystals of complexes **2b** and **2c** were obtained in the same way as for **2a**, using $[Rh(cod)_2]PF_6$ (69.0 mg, 0.15 mmol) and $[Rh(cod)_2]ClO_4$ (63.0 mg, 0.15 mmol), respectively. Single crystals of **2b** were obtained at −5 °C after 1 month, whereas crystals of **2c** were collected at −30 °C after 3 d. **2b**: Yield 59 mg (58%). Calc. for $C_{22}H_{20}F_6N_2PRh{\cdot}2C_3H_6O$: C, 49.72; H, 4.77; N, 4.14. Found: C, 47.36; H, 3.93; N, 4.72%. IR (KBr, cm^{-1}): 1603, 1487, 1421 and 833. **2c**: Yield 53 mg (52%). Calc. for $C_{22}H_{20}ClN_2O_4Rh$: C, 51.33; H, 3.92; N, 5.44. Found: C, 50.94; H, 3.59; N, 5.48%. IR (KBr, cm^{-1}): 1603, 1486, 1419 and 1091.

(e) $\{[Rh(4\text{-bpe})(cod)]BF_4{\cdot}2Me_2CO\}_n$ 3a. Acetone solutions (5 ml each) of $[Rh(cod)_2]BF_4$ (39.2 mg, 0.10 mmol) and 4-bpe (18.2 mg, 0.10 mmol) were prepared in Schlenk tubes under Ar, respectively. A 3 ml sample of each solution was layered in a 5 mm diameter glass tube, after which the tube was sealed. The solution was allowed to stand at −30 °C for 1 month and yellow crystals of **3a** were collected. Yield 40 mg (74%). Calc. for $C_{20}H_{22}N_2BF_4Rh{\cdot}2C_3H_6O$: C, 52.37; H, 5.75; N, 4.70. Found: C, 50.59; H, 4.19; N, 5.70. IR (KBr, cm^{-1}) 1611, 1505, 1429 and 1047 cm^{-1}.

(f) $\{[Rh(4\text{-bpe})(cod)]PF_6\}_n$ 3b and $\{[Rh(4\text{-bpe})(cod)]ClO_4\}_n$ 3c. The precipitates of complexes **3b** and **3c** were prepared in the same manner as for **3a**, using $[Rh(cod)_2]PF_6$ (46.0 mg, 0.10 mmol) and $[Rh(cod)_2]ClO_4$ (42.0 mg, 0.10 mmol), respectively. **3b**: Yield 49 mg (77%). Calc. for $C_{20}H_{22}F_6N_2PRh$: C, 44.63; H, 4.12; N, 5.20. Found: C, 45.24; H, 4.34; N, 4.88%. IR (KBr, cm^{-1}): 1611, 1505, 1429 and 847 cm^{-1}. **3c**: Yield 47 mg (89%). Calc. for $C_{20}H_{22}ClN_2O_4Rh$: C, 48.75; H, 4.50; N, 5.68. Found: C, 47.33; H, 4.37; N, 5.31%. IR (KBr, cm^{-1}): 1609, 1503, 1429 and 1092 cm^{-1}.

Structure determinations. X-Ray measurements of complexes **1a** and **3a** were made with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) on a Quantum CCD area detector coupled with a Rigaku AFC-7 diffractometer. For **2a** and **2b** a suitable crystal of each was attached to the end of a glass fiber and mounted on a Rigaku AFC-7R automated diffractometer equipped with graphite monochromated Mo-Kα radiation. Standard reflections decreased by 28.5% for **2b** so a linear correction factor was applied. The structures were solved by direct methods (SAPI 91[16a] for **1a**, SIR 92[16b] for **2a**, and SIR 88[16c] for **2b** and **3a**) and expanded using Fourier techniques.[17] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. For **1a** the final cycle of full-matrix least squares refinement was based on F^2 using the program SHELXL 97.[18] For **2a** the F atoms of the BF_4 anion are disordered and were refined using 75% F(3) and 25% F(4). The atomic scattering factors and anomalous dispersion terms were taken from ref. 19. All calculations were performed using the TEXSAN crystallographic software package.[20] Details of crystal data are summarized in Table 1.

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See http://www/rsc.org/suppdata/dt/1999/4357/ for crystallographic files in .cif format.

Results and discussion

Dinuclear rhodium(I) complexes

There are two molecules of $[Rh_2(2\text{-bpbd})_2(cod)_2][BF_4]_2$ **1a** and two molecules of solvated acetone in a unit cell. The structure of the cation moiety of **1a** is presented in Fig. 1(a), together with an atomic labeling scheme. Complex **1a** has an inversion center of symmetry at the midpoint of the Rh(1)···Rh(1′) vector. Each Rh atom is bonded to two N atoms of 2-bpbd and two C=C bonds of cod in a square-planar geometry. The Rh

Table 1 Crystallographic data and details of the structure determination of complexes **1a**, **2a**, **2b** and **3a**

	1a	2a	2b	3a
Formula	$C_{25}H_{26}BF_4N_2ORh$	$C_{28}H_{32}BF_4N_2O_2Rh$	$C_{28}H_{32}F_6N_2O_2PRh$	$C_{23}H_{28}BF_4N_2ORh$
Formula weight	560.20	618.23	676.44	538.20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/m$	$P2_1/m$	*Pbca*
a/Å	14.38(5)	9.162(4)	9.347(2)	15.153(3)
b/Å	10.14(4)	18.442(3)	18.114(3)	16.4660(5)
c/Å	17.62(2)	9.573(2)	9.917(3)	19.698(1)
β/°	95.24(3)	108.79(5)	108.53(2)	
U/Å^3	2557(11)	1531(1)	1592.1(6)	4914.9(7)
Z	4	2	2	8
μ(Mo-Kα)/cm^{-1}	7.14	6.06	6.46	7.40
T/K	296	296	296	296
Measured reflections	5858	3838	3989	5117
Observed reflections	4698	3624	3763	5092
$R1$	0.048	0.055	0.055	0.079
$wR2$	0.140	0.144	0.164	0.188

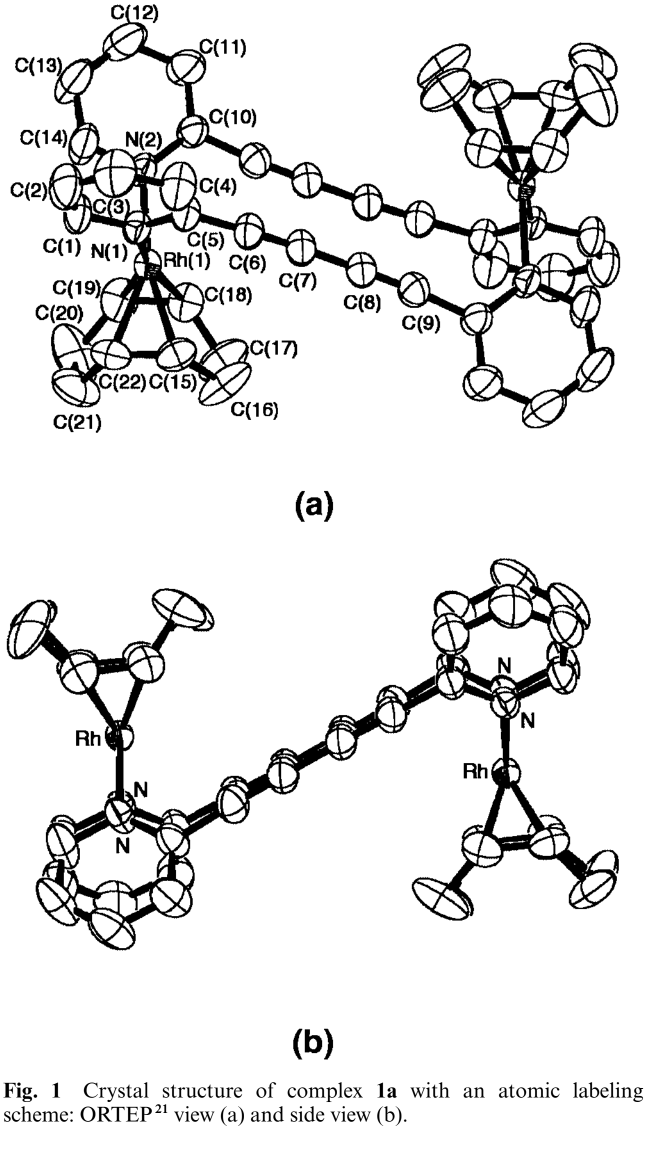

Fig. 1 Crystal structure of complex **1a** with an atomic labeling scheme: ORTEP[21] view (a) and side view (b).

Table 2 Selected bond distances (Å) and bond angles (°) of complex **1a**

Rh(1)–N(1)	2.109(4)	Rh(1)–N(2)	2.109(4)
Rh(1)–C(15)	2.119(6)	Rh(1)–C(18)	2.131(6)
Rh(1)–C(19)	2.127(5)	Rh(1)–C(22)	2.126(4)
C(5)–C(6)	1.436(7)	C(6)≡C(7)	1.185(7)
C(7)–C(8)	1.375(7)	C(8)≡C(9)	1.187(7)
C(15)=C(22)	1.374(7)	C(18)=C(19)	1.383(7)
N(1)–Rh(1)–N(2)	86.6(2)	N(1)–Rh(1)–C(15)	92.1(2)
N(1)–Rh(1)–C(18)	164.4(1)	N(1)–Rh(1)–C(19)	157.7(2)
N(1)–Rh(1)–C(22)	91.2(2)	N(2)–Rh(1)–C(15)	166.1(2)
N(2)–Rh(1)–C(18)	95.5(2)	N(2)–Rh(1)–C(19)	91.3(2)
N(2)–Rh(1)–C(22)	156.0(2)	C(15)–Rh(1)–C(18)	82.1(2)
C(15)–Rh(1)–C(19)	95.1(2)	C(15)–Rh(1)–C(22)	37.8(2)
C(18)–Rh(1)–C(19)	37.9(2)	C(18)–Rh(1)–C(22)	93.0(2)
C(19)–Rh(1)–C(22)	81.9(2)	Rh(1)–N(1)–C(1)	118.9(3)
Rh(1)–N(1)–C(5)	123.3(3)	Rh(1)–N(2)–C(10)	125.7(3)
Rh(1)–N(2)–C(14)	116.5(3)	Rh(1)–C(15)–C(16)	109.7(4)
Rh(1)–C(15)–C(22)	71.4(3)	Rh(1)–C(18)–C(17)	112.0(4)
Rh(1)–C(18)–C(19)	70.9(3)	Rh(1)–C(19)–C(18)	71.2(3)
Rh(1)–C(19)–C(20)	109.2(4)	Rh(1)–C(22)–C(15)	70.8(3)
Rh(1)–C(22)–C(21)	111.7(4)	C(5)–C(6)–C(7)	175.1(5)
C(6)–C(7)–C(8)	176.6(5)	C(7)–C(8)–C(9)	177.7(5)

atom is bridged by two 2-bpbd ligands to afford a unique dinuclear structure. The most remarkable feature is that two Rh atoms and two 2-bpbd ligands form an 18-membered $Rh_2N_4C_{12}$ framework. It is interesting that each Rh atom with the co-ordinating cod ligand is situated above and below the parallel diyne portion (Fig. 1(b)). The diyne portion of 2-bpbd has an almost linear geometry: the C(5)–C(6)–C(7), C(6)–C(7)–C(8) and C(7)–C(8)–C(9) angles are 175.1(5), 176.6(5) and 177.7(5)°, respectively. The diyne portions are in parallel 3.91 Å apart from each other. A pair of pyridyl groups are opposite each other at the N(1)–Rh(1)–N(2) angle of 86.6(2)°. Regarding 2-bpbd complexes, although the 1-D silver(I) co-ordination polymer $[Ag(2\text{-bpbd})(NO_3)]_n$[22] with linkage to tetrahedral silver(I) centers has only been reported recently, **1a** is the first reported dinuclear rhodium(I) complex with a 2-bpbd ligand. Selected bond distances and bond angles are listed in Table 2.

The average Rh–N distance of 2.109 Å is close to that (2.067(4)–2.13(1) Å) of similar four-co-ordinate rhodium(I) complexes.[23] The average Rh–C (cod) distance of 2.126 Å is within the range of those (2.07(4)–2.131(3) Å) of other rhodium(I) diene complexes.[23] Although the average C=C distance of 1.379 Å is in the range of those (1.373(16)–1.41(5) Å) of other rhodium(I) cod complexes,[23] it is slightly longer than that (1.341 Å) of metal-free cod, indicative of the contribution of π-back donation. In 2-bpbd the average C≡C distance of 1.186 Å is equal to that (1.192(3) Å) of metal-free 2-bpbd,[24] with no elongation observed in response to formation of the complex. The Rh(1)–N(1)–C(5) and Rh(1)–N(2)–C(10) angles are 123.3(3) and 125.7(3)°, respectively.

1-D Rhodium(I) co-ordination polymers

(a) Crystal structures of complexes 2a and 2b. There are two molecules of $\{[Rh(4\text{-bpbd})(cod)]X\}_n$($X = BF_4$ **2a** or PF_6 **2b**) and two molecules of solvated acetone in a unit cell. Complexes **2a** and **2b** are isomorphous. Both possess an inversion center of symmetry at the Rh(1). As a representative structure, the

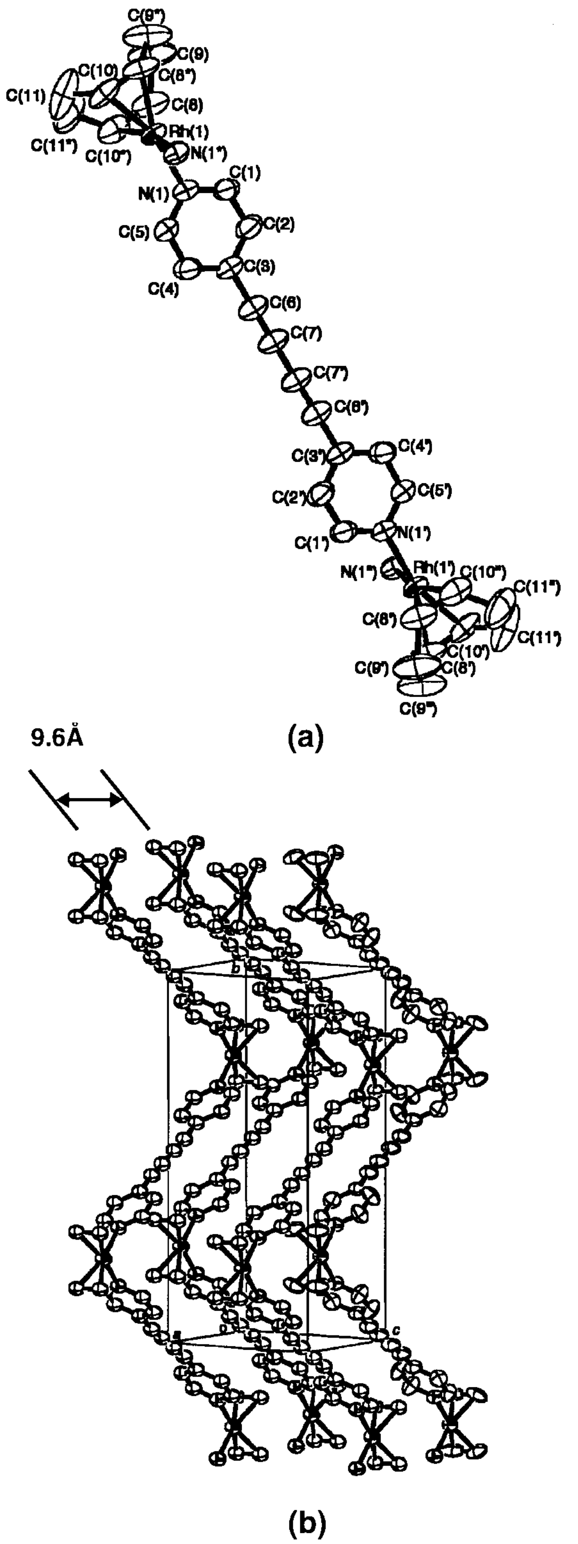

Fig. 2 Fragment structure of complex **2a** with an atomic labeling scheme (a) and molecular packing structure along the *b* axis (b).

Table 3 Selected bond distances (Å) and bond angles (°) of complex **2a**

Rh(1)–N(1)	2.106(4)	Rh(1)–C(8)	2.122(5)
Rh(1)–C(10)	2.119(5)	C(6)≡C(7)	1.191(6)
C(7)–C(7′)	1.370(9)	C(8)=C(10)	1.364(8)
N(1)–Rh(1)–N(1′)	87.0(2)	N(1)–Rh(1)–C(8)	92.9(2)
N(1)–Rh(1)–C(8′)	162.2(2)	N(1)–Rh(1)–C(10)	160.3(2)
N(1)–Rh(1)–C(10′)	91.8(2)	C(8)–Rh(1)–C(8′)	81.9(3)
C(8)–Rh(1)–C(10)	94.2(2)	C(8)–Rh(1)–C(10′)	37.5(2)
C(10)–Rh(1)–C(10′)	82.7(3)	Rh(1)–N(1)–C(1)	123.0(3)
Rh(1)–N(1)–C(5)	118.8(3)	Rh(1)–C(8)–C(9)	110.6(4)
Rh(1)–C(8)–C(10′)	71.1(3)	Rh(1)–C(10)–C(8′)	71.3(3)
Rh(1)–C(10)–C(11)	110.3(4)	C(3)–C(6)–C(7)	173.9(5)
C(6)–C(7)–C(7′)	179.4(8)		

Table 4 Selected bond distances (Å) and bond angles (°) of complex **2b**

Rh(1)–N(1)	2.116(4)	Rh(1)–C(8)	2.140(5)
Rh(1)–C(10)	2.117(5)	C(6)≡C(7)	1.200(7)
C(7)–C(7′)	1.367(9)	C(8)=C(10)	1.374(9)
N(1)–Rh(1)–N(1′)	87.0(2)	N(1)–Rh(1)–C(8)	91.7(2)
N(1)–Rh(1)–C(8′)	160.2(2)	N(1)–Rh(1)–C(10)	92.8(2)
N(1)–Rh(1)–C(10′)	162.2(2)	C(8)–Rh(1)–C(8′)	82.8(3)
C(8)–Rh(1)–C(10)	37.7(2)	C(8)–Rh(1)–C(10′)	94.4(2)
C(10)–Rh(1)–C(10′)	82.0(3)	Rh(1)–N(1)–C(1)	119.1(3)
Rh(1)–N(1)–C(5)	122.7(4)	Rh(1)–C(8)–C(9)	109.4(5)
Rh(1)–C(8)–C(10)	70.3(3)	Rh(1)–C(10)–C(8)	72.1(3)
Rh(1)–C(10)–C(11)	110.3(4)	C(3)–C(6)–C(7)	173.8(6)
C(6)–C(7)–C(7′)	179.3(9)		

fragment of **2a** is shown in Fig. 2(a), together with an atomic labeling scheme. Each Rh atom is co-ordinated to two N atoms of 4-bpbd and two C=C bonds of cod, resulting in a square-planar geometry. The Rh atom is in turn linked by 4-bpbd ligands to afford a 1-D zigzag-chain structure (Fig. 2(b)), which is formed through the linkage of square-planar rhodium(I) centers. A dinuclear tungsten(0) complex $[\{W(CO)_4(P(OPh)_3)\}_2(4\text{-bpbd})]$,[25] an interwoven 2-D sheet copper(I) co-ordination polymer $\{[Cu_2(CH_3CN)_2(4\text{-bpbd})_3](PF_6)_2\}_n$[26] and a 3-D cadmium(II) co-ordination polymer $[Cd(CN)_2(4\text{-bpbd})]_n$[27] have been reported. However, a 1-D co-ordination polymer with 4-bpbd ligand has still not been observed. As mentioned in the introduction, the reported 1-D co-ordination polymers are generally constructed through the linkage of octahedral or tetrahedral metal centers. Complexes **2a** and **2b** are the first reported 1-D zigzag-chain rhodium(I) co-ordination polymers with the linkage of square-planar rhodium(I) centers. Selected bond distances and bond angles of **2a** and **2b** are listed in Tables 3 and 4, respectively.

The average Rh–N distances of 2.106 and 2.116 Å in complexes **2a** and **2b** are similar to those (2.067(4)–2.13(1) Å) found in other four-co-ordinate rhodium(I) complexes.[23] The average Rh–C (cod) distances of 2.121 and 2.129 Å in **2a** and **2b** are close to those of other rhodium(I) diene complexes.[23] The average C=C distances of 1.364 and 1.374 Å are similar to those of other rhodium(I) cod complexes,[23] and slightly longer than that of metal-free cod, which is indicative of the contribution of the π-back donation bond. On the other hand, the average C≡C distances of 1.191 and 1.200 Å are not longer than that (1.201(6) Å) in metal-free 4-bpbd.[28] The angles of C(3)–C(6)–C(7) and C(6)–C(7)–C(7′) are 173.9(5) and 179.4(8)° and 173.8(6) and 179.3(9)° in **2a** and **2b**, respectively. Two pyridyl groups on both sides of 4-bpbd are completely coplanar through the diyne portion of the complex. Therefore, the co-ordinating 4-bpbd possesses a planar structure.

The molecular packing of complex **2a** is depicted in Fig. 2(b). As shown above, each Rh atom is linked by 4-bpbd ligands to give a 1-D zigzag-chain structure. The N(1)–Rh(1)–N(1′) angles are 87.0(2) and 87.0(2)° in **2a** and **2b**, respectively. The Rh atoms and the co-ordinating 4-bpbd are located at nearly right angles to each other. The zigzag chains are located in parallel approximately 9.6 and 9.9 Å apart in **2a** and **2b**, respectively. The counter anions (BF_4, **2a**; PF_6, **2b**) and two molecules of solvated acetone are present between the 1-D zigzag chains. No intermolecular interaction was found between the zigzag chains.

(b) Crystal structure of complex 3a. Similar to **2a** and **2b**, in complex **3a** a $\{[Rh(4\text{-bpe})(cod)]BF_4\}_n$ unit and two molecules

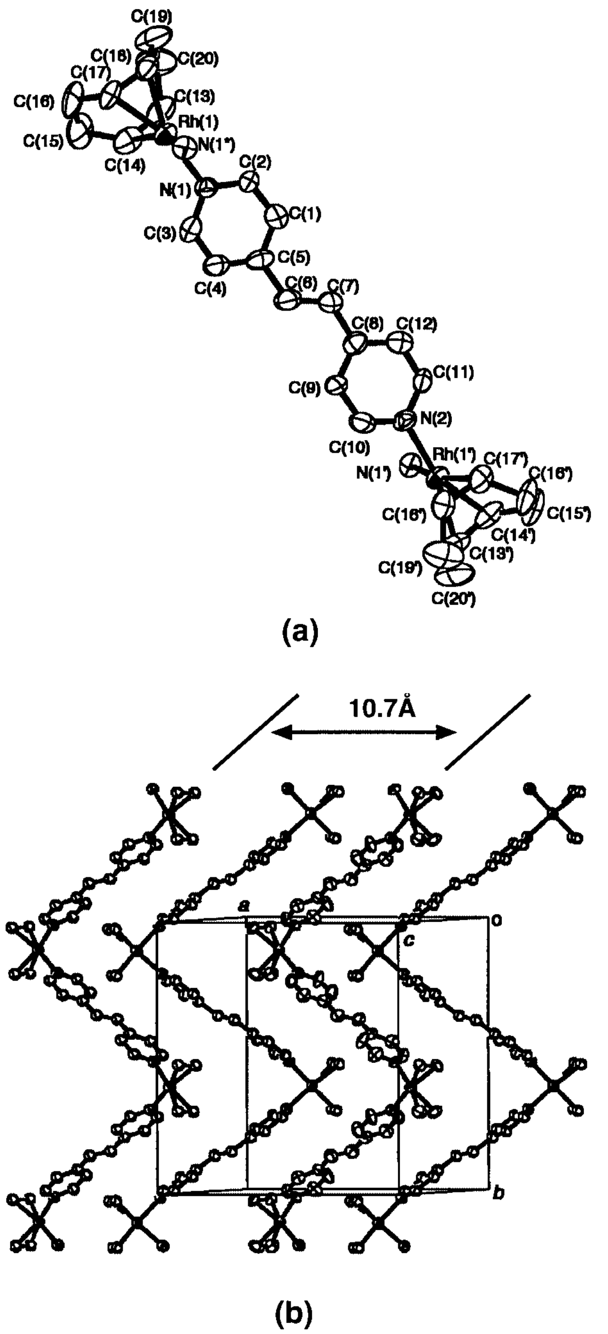

Fig. 3 Fragment structure of complex **3a** with an atomic labeling scheme (a) and molecular packing structure along the *b* axis (b).

of solvated acetone in a unit cell. Complex **3a** possesses an inversion center of symmetry at the Rh(I) atom. The fragment structure is shown in Fig. 3(a), together with an atomic labeling scheme. Each Rh atom is co-ordinated by two N atoms of 4-bpe and two C=C bonds of cod in a square-planar geometry. The square-planar centers are in turn joined by a 4-bpe ligand to provide a 1-D zigzag-chain structure (Fig. 3(b)). Our survey of 1-D co-ordination polymers with 4-bpe ligands found the copper(I) co-ordination polymer $\{[\mathrm{Cu(dmp)(4\text{-}bpe)}]\mathrm{BF_4}\}_n$ (dmp = 2,9-dimethyl-1,10-phenanthroline),[9c] the gold(I) co-ordination polymers $[\mathrm{Au(Ph_2P(CH_2)}_n\mathrm{PPh_2)(4\text{-}bpe)}]_m$ ($n = 3$ or 4),[29a] the manganese(II) co-ordination polymer $[\mathrm{Mn(hfac)(4\text{-}bpe)}]_n$ (hfac = hexafluoroacetylacetonate),[29b] and the cadmium(II) co-ordination polymer $[\mathrm{Cd(4\text{-}bpe)_{1.5}(NO_3)_2}]_n$,[29c] together with 2-D iron[4c] and manganese(II)[30] co-ordination polymers and 3-D copper(I) co-ordination polymers.[31] Recently the 1-D copper(II) co-ordination polymer with 4-bpe has been found in an integrating 3-D framework.[29d] All of these 1-D co-ordination polymers are assembled by the linkage of two-co-ordinate linear or octahedral metal centers. In addition to **2a** and **2b**, complex **3a** is a significant 1-D co-ordination polymer with the linkage of square-planar rhodium(I) centers. The selected bond distances and bond angles for **3a** are listed in Table 5.

Table 5 Selected bond distances (Å) and bond angles (°) of complex **3a**

Rh(1)–N(1)	2.097(7)	Rh(1)–N(2)	2.109(7)
Rh(1)–C(13)	2.147(8)	Rh(1)–C(14)	2.112(9)
Rh(1)–C(17)	2.144(9)	Rh(1)–C(18)	2.113(8)
C(6)=C(7)	1.30(1)	C(13)=C(14)	1.37(1)
C(17)=C(18)	1.40(1)		
N(1)–Rh(1)–N(2)	87.7(3)	N(1)–Rh(1)–C(13)	91.8(3)
N(1)–Rh(1)–C(14)	90.6(3)	N(1)–Rh(1)–C(17)	162.9(3)
N(1)–Rh(1)–C(18)	158.7(4)	N(2)–Rh(1)–C(13)	166.1(4)
N(2)–Rh(1)–C(14)	156.5(4)	N(2)–Rh(1)–C(17)	92.6(3)
N(2)–Rh(1)–C(18)	93.3(3)	C(13)–Rh(1)–C(14)	37.4(4)
C(13)–Rh(1)–C(17)	91.9(4)	C(13)–Rh(1)–C(18)	82.1(3)
C(14)–Rh(1)–C(17)	82.3(4)	C(14)–Rh(1)–C(18)	96.6(4)
C(17)–Rh(1)–C(18)	38.4(4)	Rh(1)–N(1)–C(2)	120.6(6)
Rh(1)–N(1)–C(3)	121.8(5)	Rh(1)–N(2)–C(10)	122.3(6)
Rh(1)–N(2)–C(11)	120.2(5)	Rh(1)–C(13)–C(14)	69.9(5)
Rh(1)–C(13)–C(20)	111.4(6)	Rh(1)–C(14)–C(13)	72.7(6)
Rh(1)–C(14)–C(15)	110.5(6)	Rh(1)–C(17)–C(16)	109.9(6)
Rh(1)–C(17)–C(18)	69.6(6)	Rh(1)–C(18)–C(17)	72.0(5)
Rh(1)–C(18)–C(19)	110.8(5)	C(5)–C(6)–C(7)	128.0(9)
C(6)–C(7)–C(8)	124.3(8)		

The average Rh–N distance of 2.103 Å is within the range of those of general four-co-ordinate rhodium(I) complexes.[23] The average Rh–C (cod) distance of 2.129 Å is similar to those of other rhodium(I) complexes.[23] The average C=C distance of 1.39 Å is slightly longer than that of metal-free cod, indicative of the existence of π-back donation. On the other hand, the average C=C distance of 1.30 Å in 4-bpe is equal to that (1.293(9) Å) in metal-free 4-bpe•TCNQ.[32] The dihedral angles defined by {C(5), C(6) and C(7)} and {C(6), C(7) and C(8)} are 0.77°, and those defined by {C(1), C(4), C(5) and C(6)} and {C(7), C(8), C(9) and C(12)} are 2.25°. The torsion angles between the two pyridyl groups of 4-bpe through the C=C bond are also 1.53°. The co-ordinating 4-bpe has a planar structure. The Rh atom and the 4-bpe are located at right angles to each other at the N(1)–Rh(1)–N(2) angle of 87.7(3)°.

The molecular packing of complex **3a** is shown in Fig. 3(b). It is interesting that the packing mode is slightly different from those of **2a** and **2b** due to the differences in the co-ordination direction of each pyridyl group. A pair of zigzag chains 10.7 Å apart is alternately aligned in a unit cell. The two counter anions $\mathrm{BF_4}$ and two molecules of solvated acetone are situated between the 1-D zigzag chains.

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