Mixed-bridged Bimetallic d^8 Complexes. Crystal and Molecular Structure of $(\eta^3\text{-}C_3H_5)Pd(\mu\text{-pz})(\mu\text{-}N_3)Rh(CO)_2$, Heterobinuclear Complex with Extended Rh···Rh Interactions

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Abstract

The preparation and properties of binuclear complexes containing the pyrazolate and azide groups as bridging ligands are reported. Representative formulae are: $M_2(\mu\text{-pz})(\mu\text{-}N_3)(CO)_4$, $M_2(\mu\text{-pz})(\mu\text{-}N_3)(COD)_2$ (M = Rh or Ir), $(CO)_2Rh(\mu\text{-pz})(\mu\text{-}N_3)ML_2$ (M = Rh, L_2 = COD, M = Ir, L = CO) and $(\eta^3\text{-}C_3H_5)Pd(\mu\text{-pz})(\mu\text{-}N_3)Rh(CO)_2$. The crystal and molecular structure of the latter complex has been determined by single-crystal X-ray methods. Crystals are monoclinic, space group $C2/c$ with cell constants a = 18.4750(10), b = 10.0351(3), c = 13.6399(6) Å, α = 90, β = 100.022(4), γ = 90°, and Z = 8. The final R and R_w values were 0.051 and 0.062 for 1417 observed reflexions. This binuclear compound packs in the crystal zig-zag chains of rhodium atoms, along the c axis, with intermolecular Rh···Rh contacts of 3.290(1) and 3.604(1) Å. The Rh···Rh···Rh angle is 163.16(4)°.

Introduction

Several mononuclear bis-(carbonyl)-rhodium(I) or iridium(I) complexes exhibiting columnar stacking have been reported [1-5]. In particular M(acac)-$(CO)_2$ compounds show properties characteristic of a semiconductor [5]. Very recently, some tri- or binuclear complexes containing $Rh(CO)_2$ moieties in a 'M(μ-az)(μ-Cl)Rh' core (az = triazolate [6], pyrazolate [7]) have been described, in which stacking arrangements of square-planar Rh units are present. Of particular interest is the use of sterically undemanding and/or planar ligands, and herein we report the preparation and properties of new binuclear complexes containing the pyrazolate (pz) and azide groups as bridging ligands [$M(\mu\text{-pz})(\mu\text{-}N_3)M'$ core], as well as the X-ray structure of $(\eta^3\text{-}C_3H_5)Pd(\mu\text{-pz})(\mu\text{-}N_3)Rh(CO)_2$, an unusual example of molecular stacking in a heterobimetallic compound.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer (range 4000-200 cm^{-1}) using Nujol mulls between polyethylene sheets or dichloromethane solutions in NaCl windows. The C, H and N analyses were carried out with a Perkin-Elmer 240B microanalyzer. ^1H NMR spectra were recorded in $CDCl_3$ solutions at room temperature on a Varian XL 200 spectrophotometer, using $SiMe_4$ as internal standard. Molecular weights were determined with a Knauer osmometer using chloroform solutions. Solvents were dried and distilled before using.

Preparation of the Mixed-bridged Bimetallic d^8 Complexes

Preparation of $Rh_2(\mu\text{-pz})(\mu\text{-}N_3)(CO)_4$ (1)

Method A. To a solution of $RhCl(CO)_2(Hpz)$ (60 mg, 0.17 mmol) in 20 ml of methanol, NaN_3 (13 mg, 0.2 mmol) was added. The green complex precipitated spontaneously. After stirring for 15 min, the suspension was evaporated to *ca.* 10 ml, and methanol:water (1:2) (10 ml) was added. The solid which separated out was filtered off, washed with methanol:water (1:2) and air dried.

Method B. To a solution of $RhCl(CO)_2(Hpz)$ (60 mg, 0.17 mmol) in 20 ml of methanol, Rh(acac)-$(CO)_2$ (48.3 mg, 0.17 mmol) was added. After stirring for 15 min, NaN_3 (13 mg, 0.2 mmol) was

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added and the complex precipitated spontaneously. The solid which separated was isolated as above. Yield: 70%. IR ν(CO)*(dichloromethane): 2020(vs), 2080(vs) and 2100(s) cm^{-1}. Molecular weight: Calc. 426, Found 439. *Anal.* Calc. for $C_7H_3N_5O_4Rh_2$: C, 19.73; H, 0.71; N, 16.44. Found: C, 19.46; H, 0.88; N, 16.63%.

Preparation of $Ir_2(\mu\text{-}pz)(\mu\text{-}N_3)(CO)_4$ *(2)*

To a solution of $IrCl(CO)_2(Hpz)$ (70.6 mg, 0.16 mmol) in 25 ml of methanol, $Ir(acac)(CO)_2$ (55.5 mg, 0.16 mmol) and NaN_3 (13 mg, 0.2 mmol) were added. After stirring and heating it to 50 °C a golden complex precipitated spontaneously. The resulting suspension was concentrated under vacuum to *ca.* 15 ml. The solid which separated out was filtered off, washed with methanol:water (1:2) and air-dried. Yield: 65%. IR ν(CO)(dichloromethane): 2000(vs), 2065(vs) and 2110(s) cm^{-1}. *Anal.* Calc. for $C_7H_3N_5O_4Ir_2$: C, 13.88; H, 0.50; N, 11.56. Found: C, 13.96; H, 0.61; N, 11.34%.

Preparation of $Rh_2(\mu\text{-}pz)(\mu\text{-}N_3)(COD)_2$ *(3)*

To a solution of $RhCl(COD)(Hpz)$ (50.3 mg, 0.16 mmol) in 20 ml of methanol, $Rh(acac)(COD)$ (49.6 mg, 0.16 mmol) and NaN_3 (13 mg, 0.2 mmol) were added. The expected complex precipitated spontaneously. The resulting suspension was concentrated to *ca.* 10 ml, and methanol:water (1:2) (20 ml) was added. The yellow solid which separated out was filtered off, washed with methanol:water (1:2) and air dried. Yield: 80%. Molecular weight: Calc. 531, Found 522. *Anal.* Calc. for $C_{19}H_{27}N_5Rh_2$: C, 42.95; H, 6.02; N, 13.18. Found: C, 42.53; H, 5.98; N, 12.90%.

Preparation of $Ir_2(\mu\text{-}pz)(\mu\text{-}N_3)(COD)_2$ *(4)*

To a solution of $Ir_2(\mu\text{-}Cl)_2(COD)_2$ (50 mg, 0.074 mmol) in 20 ml of dichloromethane Hpz (10.1 mg, 0.15 mmol) was added. The colour of the solution changed from orange to pale yellow. After stirring for 15 min, the solution containing $IrCl(COD)(Hpz)$ was evaporated under vacuum and dissolved in 20 ml of methanol. $Ir(acac)(COD)$ (60 mg, 0.15 mmol) and NaN_3 (12 mg, 0.18 mmol) were added to give a yellow precipitate, which was collected by filtration and washed with cold methanol. Yield: 65%. *Anal.* Calc. for $C_{19}H_{27}N_5Ir_2$: C, 32.15; H, 2.83; N, 9.86. Found: C, 31.61; H, 3.43; N, 9.66%.

Preparation of $(COD)Rh(\mu\text{-}pz)(\mu\text{-}N_3)Rh(CO)_2$ *(5)*

To a solution of $RhCl(COD)(HPz)$ (50.3 mg, 0.16 mmol) in 20 ml of methanol, $Rh(acac)(CO)_2$ (41.3 mg, 0.16 mmol) and NaN_3 (13 mg, 0.2 mmol) were added. After stirring for 30 min, the suspension was evaporated to dryness. The residue was extracted with 15 ml of dichloromethane and the solution was concentrated to *ca.* 3 ml. Addition of diethylether gave the orange complex. The solid which separated out was filtered off, washed with diethylether and air dried. Yield: 65%. IR ν(CO)(dichloromethane): 2010(vs), 2055(vs) and 2087(vs) cm^{-1}. Molecular weight: Calc. 479, Found 529. *Anal.* Calc. for $C_{13}H_{15}N_5O_2Rh_2$: C, 32.59; H, 3.15; N, 14.62. Found: C, 32.92; H, 3.33; N, 14.44%.

Preparation of $(\eta^3\text{-}C_3H_5)Pd(\mu\text{-}pz)(\mu\text{-}N_3)Rh(CO)_2$ *(6)*

To a solution of $PdCl(\eta^3\text{-}C_3H_5)(Hpz)$ (42.7 mg, 0.17 mmol) in 15 ml of methanol, $Rh(acac)(CO)_2$ (43.8 mg, 0.17 mmol) and NaN_3 (13 mg, 0.2 mmol) were added. The red complex precipitated spontaneously and was isolated as above. Yield: 80%. IR ν(CO)(dichloromethane): 2010(vs), 2060(vs) and 2090(vs) cm^{-1}. Molecular weight: Calc. 415, Found 408. *Anal.* Calc. for $C_8H_8N_5O_2RhPd$: C, 23.13; H, 1.94; N, 16.85. Found: C, 23.16; H, 1.83; N, 17.10%.

Preparation of $(CO)_2Rh(\mu\text{-}pz)(\mu\text{-}N_3)Ir(CO)_2$ *(7)*

To a solution of $RhCl(CO)_2(Hpz)$ (52.5 mg, 0.2 mmol) in 25 ml of methanol, $Ir(acac)(CO)_2$ (69.5 mg, 0.2 mmol) and NaN_3 (15 mg, 0.23 mmol) were added. A mixture of **1**, **2** and **7** precipitated spontaneously. The suspension was concentrated to dryness on a rotary evaporator. The residue was extracted with 20 ml of dichloromethane and filtered off (**2** was withdrawn). The resulting solution was concentrated to *ca.* 5 ml and the addition of diethylether (20 ml) gave a green complex, which was collected by filtration and washed with diethylether (**1** was retired). Yield: 65%. IR ν(CO)(dichloromethane): 2000(s), 2020(vs), 2065(s), 2080(vs) and 2110(s) cm^{-1}. *Anal.* Calc. for $C_7H_3N_5O_4RhIr$: C, 16.28; H, 0.58; N, 13.56. Found: C, 16.91; H, 0.56; N, 13.69%.

Preparation of $Pd_2(\mu\text{-}pz)(\mu\text{-}N_3)(\eta^3\text{-}C_3H_5)_2$ *(8)*

To a solution of $PdCl(\eta^3\text{-}C_3H_5)(Hpz)$ (60 mg, 0.24 mmol), in 20 ml of methanol, NaN_3 (17 mg, 0.26 mmol) was added. The white complex precipitated spontaneously. After stirring for 10 min, the suspension was evaporated to *ca.* 10 ml, and methanol:water (1:2) (10 ml) was added. The solid which separated out was filtered off, washed with methanol:water (1:2) and air dried. Yield: 80%. *Anal.* Calc. for $C_9H_{13}N_5Pd_2$: C, 26.75; N, 3.24; N, 17.33. Found: C, 26.85; H, 3.31; N, 17.86%.

X-ray Crystallographic Procedures

The data crystal and data collection parameters as well as the solution and refinement characteristics

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*For all the mixed-bridged carbonyl complexes azide vibrations are reported together with ν(CO).

TABLE I. Crystal Analysis Parameters at Room Temperature

Crystal Data	
Formula	$C_8H_8N_5O_2RhPd$
Crystal habit	Prismatic, brown
Crystal size (mm)	0.06 × 0.18 × 0.32
Symmetry	monoclinic, $C2/c$
Unit cell dimensions	$a = 18.4750(10)$, $b = 10.0351(3)$, $c = 13.6399(6)$ Å, $\alpha = 90$, $\beta = 100.022(4)$, $\gamma = 90°$
Packing: V (Å^3), Z	2490.2(2), 8
D_c (g cm^{-3}), M $F(000)$	2.216, 415.49, 1584
μ (cm^{-1})	229.62
Experimental data	
Technique	$\omega/2\theta$ scans scan width: 1.5°, detector apertures 1 × 1, up to $\theta_{max} = 65°$ 1 min./reflex.
Number of reflexions	
Independent	2096
Observed	1417 ($3\sigma(I)$ criterion)
Abs. correction	Min–max transmission factors: 0.03–0.31
Solution and refinement parameters	
Number of variables	154 (H atoms fixed)
Degrees of freedom	1263
Ratio of freedom	9.2
Final shift/error	0.05
Max. thermal value	$U11(C13) = 0.22(3)$ Å^2
Final ΔF peaks	1.0 e Å^{-3} near the Rh atom
Final R and R_w	0.051, 0.62

are summarized in Table I. The orientation matrix and the unit cell size and shape were obtained by least squares fit from 73 reflections ($2 < \theta < 45°$). Two standard reflections, monitored every 90 min, gave no significant variation over the whole data collection on a Philips PW 1100 diffractometer, with bisecting geometry and graphite oriented monochromator for the employed Cu Kα radiation. Polyhedral absorption correction was used [8]. The position of the two metal atoms were located in a Patterson map, and the remaining non-hydrogen atoms were located in a difference Fourier calculation. The whole atomic set was refined anisotropically in a full matrix least squares calculation on F(obs). All hydrogen atoms were located in a difference synthesis and included isotropically in the last cycles of the refinement, but were kept fixed, where an empirical weighting scheme was employed so as to give no trends on $\langle w\Delta^2 F\rangle$ when analyzed *versus* $\langle |F(\text{obs})| \rangle$ or $\langle \sin\theta/\lambda \rangle$. No reflections significantly affected by extinction were found. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography [9]. All calculations were performed on a VAX 11/750 and most of them were done using the XRAY 76 [8] system of programs.

Results and Discussion

The mononuclear complex $RhCl(CO)_2(Hpz)$ [6] reacts with sodium azide to give the binuclear compound $Rh_2(\mu\text{-pz})(\mu\text{-}N_3)(CO)_4$ as a green solid with a metallic sheen. A general synthetic strategy for the preparation of $L_2M(\mu\text{-pz})(\mu\text{-}N_3)M'L'_2$ complexes is shown in eqn. (1)

$$\tfrac{1}{2}M_2(\mu\text{-Cl})_2(L_2)_2 \xrightarrow{Hpz} MCl(L_2)(Hpz) \xrightarrow[-Hacac,\ -NaCl]{M'(acac)L'_2,\ NaN_3} L_2M(\mu\text{-pz})(\mu\text{-}N_3)M'L'_2 \qquad (1)$$

Complex	L_2	M	M′	L'_2
1	$(CO)_2$	Rh	Rh	$(CO)_2$
2	$(CO)_2$	Ir	Ir	$(CO)_2$
3	COD	Rh	Rh	COD
4	COD	Ir	Ir	COD
5	COD	Rh	Rh	$(CO)_2$
6	$\eta^3\text{-}C_3H_5$	Pd	Rh	$(CO)_2$

Table II collects representative ^1H NMR data for the complexes **1**–**6** (and **7**, see below). The solid IR spectra of the carbonyl compounds **1**–**2** and **5**–**7**

TABLE II. ^1H NMR Chemical Shifts[a] (ppm)[b] and Linewidths (Hz)[c] for the Compounds in $CDCl_3$, 293 K

Compound	pz			COD or (η^3-C_3H_5)		
	H3	H5	H4			
1	7.55(d, 2.2)		6.23(t, 2.2)			
2	7.79(d, 2.2)		6.29(t, 2.2)			
3	6.83(d, 2.1)		6.06(t, 2.1)	>CH, 3.75(d, 2.5) >CH, 4.25(d, 2.7)	>CH_2, 1.91(m) >CH_2, 2.49(m)	
4	7.15(d, 2.3)		6.19(t, 2.3)	>CH, 3.54(d, 2.6) >CH, 3.94(d, 2.8)	>CH_2, 1.69(m) >CH_2, 2.31(m)	
5	7.23(d, 2.2)	6.94(d, 2.2)	6.16(t, 2.2)	>CH, 3.87(d, 2.7) >CH, 4.28(d, 2.6)	>CH_2, 1.95(m) >CH_2, 2.53(m)	
6	7.56(d, 2.1)	7.40(d, 2.1)	6.19(t, 2.1)	H_{anti}, 2.98(d, 12) H_{anti}, 3.19(d, 12)	H_{syn}, 3.67(d, 6.8) H_{syn}, 3.84(d, 6.8)	H, 5.67(m)
7	7.73(d, 2.1)	7.58(d, 2.1)	6.25(t, 2.1)			

[a] Position of the center of the doublet (d), triplet (t) or multiplet (m). [b] The chemical shifts are relative to Me_4Si. [c] The linewidth in Hz is given in parentheses.

are rather complex. This observation along with the dark colour and metallic lustre of some of the complexes suggest extended metal–metal interactions, which were confirmed by X-ray methods for complex **6**. The latter compound was obtained according to eqn. (1), along with small amounts of **1** and $Pd_2(\mu$-pz)(μ-N_3)(η^3-C_3H_5)$_2$ (**8**) (independently prepared by reacting PdCl(η^3-C_3H_5)(Hpz) with NaN_3). On the other hand ^1H NMR studies on the products obtained by reacting $RhCl(L_2)(Hpz)$ with $Ir(acac)(L_2)$ (L_2 = COD or $(CO)_2$), show the presence of a mixture of **3**, **4** and presumably (COD)Rh(μ-pz)(μ-N_3)Ir(COD) (**9**) (*ca.* 1:1:2) for L_2 = COD (see Fig. 1), and **1**, **2** and $(CO)_2$Rh(μ-pz)(μ-N_3)Ir$(CO)_2$ (**7**) for L = CO. Attempts at separation of complex **9** from the mixture were unsuccessful, but complex **7** was isolated by taking advantage of the different solubility of the compounds. Heterobimetallic d^8 complexes with bridging nitrogen donor ligands are generally difficult to isolate due to their tendency to undergo redistribution reactions [10]. However we have previously reported some azolate Rh(I)–M(II) (M = Pt [11, 12a] or Pd [12, 13]) d^8 complexes as well as several heteronuclear d^8–d^6 compounds of rhodium, iridium and ruthenium [14–16].

TABLE III. Final Atomic Coordinates

Atom	*x/a*	*y/b*	*z/c*
Rh	0.01383(5)	−0.00261(9)	0.12242(6)
Pd	−0.12434(6)	−0.24997(11)	0.13085(7)
N1	−0.0956(7)	0.0450(11)	0.1109(8)
N2	−0.1479(6)	−0.0519(14)	0.1179(9)
C3	−0.2129(9)	0.0133(26)	0.1131(12)
C4	−0.2038(13)	0.1440(25)	0.1055(14)
C5	−0.1288(11)	0.1650(17)	0.1053(11)
N6	−0.0181(6)	−0.2011(10)	0.1094(9)
N7	0.0238(7)	−0.2917(11)	0.0952(9)
N8	0.0624(10)	−0.3745(14)	0.0826(13)
C9	0.0431(11)	0.1722(14)	0.1344(12)
O9	0.0621(10)	0.2796(11)	0.1477(11)
C10	0.1110(8)	−0.0512(15)	0.1357(10)
O10	0.1707(6)	−0.0857(12)	0.1406(9)
C11	−0.2257(15)	−0.3366(33)	0.1405(24)
C12	−0.1716(20)	−0.4193(33)	0.1808(25)
C13	−0.1173(20)	−0.4627(20)	0.1344(23)

The structure of complex **6** is shown in Fig. 2, with the numbering scheme used in the crystallographic work which corresponds to that of the final coordinates that appear in Table III, for the non hydrogen atoms. Selected geometrical parameters describing the structure are given in Tables IV and V. Both metal atoms present a distorted square planar coordination. The distortion may be described by the dihedral angles given in Table V and the angles

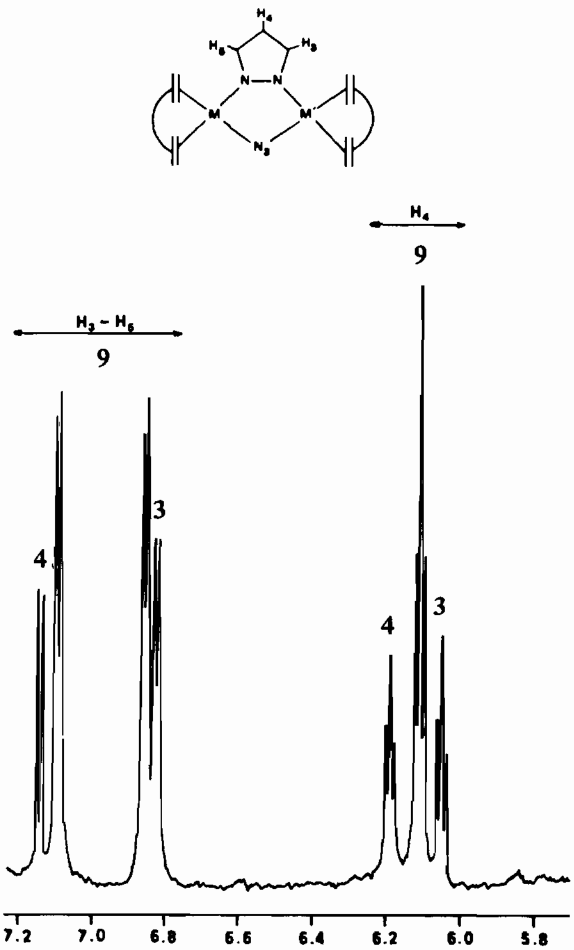

Fig. 1. ^{1}H NMR in the δ 5.8–7.2 range (pyrazolate protons) for the products obtained by reacting RhCl(COD)(Hpz) with Ir(acac)(COD) (complexes **3**, **4** and **9**).

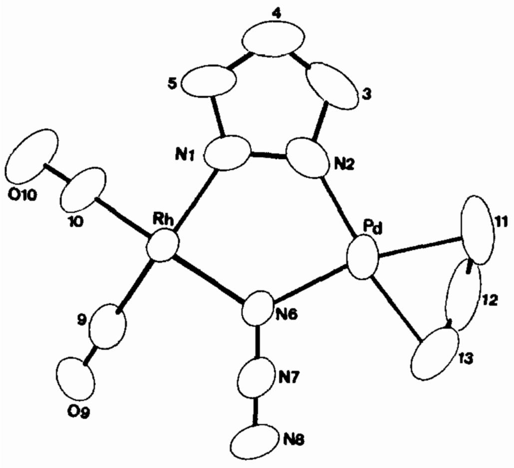

Fig. 2. An ORTEP view of the complex, with 30% probability ellipsoids showing the numbering scheme.

TABLE IV. Bond Lengths (Å) and Angles (°)

Rh–N1	2.057(12)	Pd–N2	2.036(14)
Rh–N6	2.076(10)	Pd–N6	2.093(11)
Rh–C9	1.834(14)	Pd–C11	2.089(29)
Rh–C10	1.838(16)	Pd–C12	2.078(35)
		Pd–C13	2.138(21)
N1–N2	1.386(17)		
N2–C3	1.358(23)	C9–O9	1.138(18)
N1–C5	1.347(21)	C10–O10	1.147(19)
C3–C4	1.329(36)	C11–C12	1.341(44)
C4–C5	1.401(32)	C12–C13	1.348(52)
N6–N7	1.231(16)	N7–N8	1.127(20)
Rh–Pd	3.577(1)	Rh–N6–Pd	118.2(5)
N1–Rh–N6	87.5(4)	N2–Pd–N6	87.2(4)
N1–Rh–C9	93.2(6)	N2–Pd–C11	103.4(9)
N1–Rh–C10	177.7(5)	N2–Pd–C13	171.0(10)
N6–Rh–C9	179.3(7)	N6–Pd–C11	168.3(9)
N6–Rh–C10	90.7(6)	N6–Pd–C13	100.5(8)
C9–Rh–C10	88.7(8)	C11–Pd–C13	68.6(11)
Rh–N1–N2	121.3(9)	Pd–N2–N1	123.4(9)
Rh–N1–C5	130.0(11)	Pd–N2–C3	130.4(12)
Rh–C9–O9	176.0(15)		
Rh–C10–O10	177.0(13)	Pd–N6–N7	118.7(9)
Rh–N6–N7	123.0(9)	C11–C12–C13	124.7(31)
N1–N2–C3	106.2(15)	N2–C3–C4	110.9(17)
C3–C4–C5	106.7(20)	C4–C5–N1	107.8(16)
C5–N1–N2	108.4(13)		
		N6–N7–N8	179.7(15)

at the metal atoms. The separation between metals, 3.577(1) Å, is shorter than the Rh–Rh separation of 3.715(2) Å found in a similar complex with chlorine as bridging ligand [17]. The central five membered ring involving the two metal atoms is puckering in a half chair conformation, with a pseudo two fold axis through N2 and the mid point of Rh–N6 (see Table V). The N6 environment is planar (angles around it adding 359.9(14)°) and the azide group is linear as observed in a related heterobridged pentamethylcyclopentadienyl rhodium(III) complex [18].

The molecules of the complex pack in the crystal in zig-zag chains of rhodium atoms, in the direction of the *c* axis around symmetry centers and two fold axes (see Fig. 3). This stacking arrangement exhibits intermolecular Rh···Rh contacts of 3.290(1) Å and 3.604(1) Å between symmetry centers and two fold axes respectively, which form an angle of 163.16(4)°. These values are comparable with that of 3.5107(8) and 3.6201(8) observed for $Rh_2(\mu\text{-pz})(\mu\text{-Cl})(CO)_4$ [7], and 3.253 and 3.271 for Rh(acac)-

TABLE V. Conformational Characteristic (°)

(a) Torsion angles

N1–N2–Pd–N6	–6.2(10)	N2–Pd–N6–Rh	14.4(6)
Pd–N6–Rh–N1	–15.8(6)	N6–Rh–N1–N2	11.9(10)
Rh–N1–N2–Pd	–4.2(14)		
N2–N1–Rh–C9	–167.9(11)	N1–N2–Pd–C11	179.0(13)
N1–Rh–N6–N7	168.4(11)	N2–Pd–N6–N7	–169.6(10)

(b) Least-squares planes through

i: (N1, N2, C3, C4, C5)
ii: (N1, N2, Pd)
iii: (N1, Rh, N6)
iv: (C9, Rh, C10)
v: (N2, Pd, N6)
vi: (C11, Pd, C13)
vii: (C11, C12, C13)

(c) Dihedral angles

iii–iv	1.4(5)	v–vi	5.9(9)
		vi–vii	66.1(34)
ii–iii	10.3(7)		
ii–vii	64.5(35)	ii–v	6.2(10)
i–ii	0.8(9)	i–iii	9.5(6)
i–v	6.9(6)	i–vii	65.4(35)

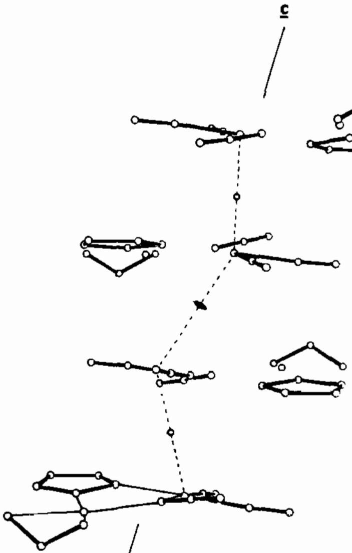

Fig. 3. Packing arrangement in crystals of the complex showing the rhodium–rhodium interactions.

$(CO)_2$ [1]; the latter complex exhibits semiconductor properties [5].

Supplementary Material

Tables of anisotropic thermal parameters, parameters for the hydrogen atoms, and observed and calculated structure factors can be obtained from the Editor-in-Chief in Padua on request.

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