Mononuclear Rhodium(I) Complexes of 4-Amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole. Crystal Structure of $[Rh(CO)_2(NH_2bpt)]ClO_4$

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Abstract

Reaction of 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (NH_2bpt) or its potassium salt (KNHbpt) with several rhodium(I) compounds, produces new neutral and cationic complexes of Rh(I). One of the complexes $[Rh(CO)_2(NH_2bpt)]ClO_4$ has been characterized by single-crystal X-ray diffraction. The crystals are monoclinic, space group $P2_1/n$, with $a = 17.6130(6)$, $b = 11.3072(2)$, $c = 9.0013(2)$ Å, $\beta = 101.536(2)°$ and $Z = 4$. The structure has been refined to $R = 0.049$.

Introduction

Rhodium complexes with 1,2- and 2,4-bridging 1,2,4-triazole units have been recently investigated [1–3]. Interestingly, the undemanding and planar ligand 1,2,4-triazole is adequate for promoting extended metal–metal interactions [1–3]. Furthermore, some rhodium(I) complexes of polyfunctional diazine ligands have been reported [4].

In addition, the coordination chemistry of the chelating triazole ligand, 4-amino-3,5-bis(pyridyn-2-yl)-1,2,4-triazole (NH_2bpt), towards nickel and cobalt has been recently studied [5]. In this context, we have now focussed our attention on this unusual ligand, which has the appropriate features to behave as a bidentate chelating anionic or neutral group towards rhodium(I). The resulting new compounds are described in this paper, including a crystal structure determination of a representative compound.

Results and Discussion

Addition of solid $[Rh_2Cl_2(diolefin)_2]$ to a solution of the ligand 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole (NH_2bpt) and potassium hydroxide, gives neutral complexes of the type [Rh(NHbpt)(diolefin)] [diolefin = tetrafluorobenzobicyclo[2,2,2]octatriene (tfb), 1.5-cyclooctadiene (cod) and bicyclo[2,2,1]heptadiene (nbd)] (compounds **I–III**).

After working-up the compounds are isolated as air-stable yellow or orange microcrystalline solids in good yield. The infrared spectra of complexes **I–III** show a sharp band due to ν(N–H) in the 3280–3230 cm^{-1} region. An alternative route, used for the synthesis of complex **I**, involves the reaction of [Rh(acac)(tfb)] with the ligand. This synthetic strategy is based on the ability of ligands containing N–H bonds (e.g. 1,2,4-triazole[1,3], 1,8-diaminonaphthalene [6,7]) to abstract the acetylacetonate group from $[Rh(acac)(L_2)]$ complexes.

A related complex of formula $[Rh(NHbpt)(CO)(PPh_3)]$ (**IV**) (ν(CO): 1960 cm^{-1}) has been prepared by reacting *trans*-$[Rh_2Cl_2(CO)_2(PPh_3)_2]$ with the ligand NH_2bpt and potassium hydroxide.

Compounds **I–IV** are non-electrolytes in acetone (Table I). The ^1H NMR data for the free ligand and some of the complexes are given in Table II.

The ^1H NMR spectrum for the free ligand in $CDCl_3$ solution shows the 10 protons while in d_6-acetone solution one of the $-NH_2$ protons cannot be located. The spectra of the complexes show that the protons of both pyridine groups are unequivalent which would indicate that the rhodium ion is most probably in a square-planar arrangement with the NHbpt groups acting as a chelate via the amine nitro-

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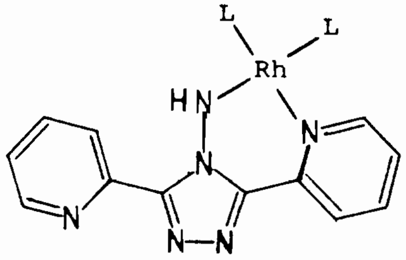
TABLE I. Colour, Analytical Results, Conductance, Yields and Spectroscopic Data for the New Complexes

Compound		Colour	Yield (%)	Analyses (%) (found(calc.)) N	C	H	Λ_M[a]	ν(NH) ν(C=C) and (C=N) cm^{-1}
I	$[Rh(tfb)(NHbpt)]$	yellow	82	14.85	50.07	2.60	–	3220
				(14.83)	(50.90)	(2.67)		1558, 1565, 1592, 1608
II	$[Rh(cod)(NHbpt)]$	orange	78	18.25	53.08	4.57	4	3240
				(18.73)	(53.58)	(4.72)		1555, 1567, 1580, 1600
III	$[Rh(nbd)(NHbpt)]$	orange	75	18.60	50.66	4.08	6	3280
				(19.4)	(52.7)	(3.93)		1556, 1567, 1590, 1602
IV	$[Rh(CO)(PPh_3)(NHbpt)]\cdot 0.5Cl_2H_2$	yellow	80	12.43	55.53	3.78	–	3260, ν(CO) 1960
				(12.49)	(56.26)	(3.74)		1560, 1565, 1590, 1602
V	$[Rh(tfb)(NH_2bpt)]ClO_4$	orange	76	13.03	43.19	2.45	116	3250
				(12.84)	(43.09)	(2.39)		1570, 1587, 1606
VI	$[Rh(cod)(NH_2bpt)]ClO_4$	orange	85	15.24	43.26	3.95	106	3240
				(15.30)	(43.72)	(4.01)		1570, 1589, 1600
VII	$[Rh(nbd)(NH_2bpt)]ClO_4$	orange	91	14.85	41.55	3.47	115	3270
				(15.76)	(42.79)	(3.37)		1575, 1590, 1608
VIII	$[Rh(CO)(PPh_3)(NH_2bpt)]ClO_4$	yellow	75	11.42	50.52	3.34	146	3220, ν(CO) 2000
				(11.49)	(50.84)	(3.45)		1570, 1590, 1608
IX	$[Rh(CO)_2(NH_2bpt)]ClO_4$	green–blue	70	16.22	33.87	1.97	132	3230, ν(CO) 2040, 2100
				(16.91)	(33.82)	(2.01)		1570, 1590, 1608
X	$[RhCl(tfb)(NH_2bpt)]$	red	46	14.16	47.29	2.63	33[b]	3200
				(13.93)	(47.82)	(2.67)		1570, 1592, 1606
XI	$[RhCl(nbd)(NH_2bpt)]$	red	60	18.03	48.78	3.97	–	3245
				(17.92)	(48.84)	(3.87)		1565, 1590, 1605

[a] Acetone solvent (in ohm^{-1} cm^2 mol^{-1}). [b] Nitromethane solvent.

gen and one of the pyridine nitrogens [N(1′) or N(1″)], as shown in the figure



The neutral complexes **I** and **II** react with protonic acids such as perchloric acid to give cationic compounds $[Rh(NH_2bpt)(diolefin)]ClO_4$ (eqn. (1))

$$[Rh(NHbpt)(diolefin)] \xrightarrow{HClO_4} [Rh(NH_2bpt)(diolefin)]ClO_4 \qquad (1)$$

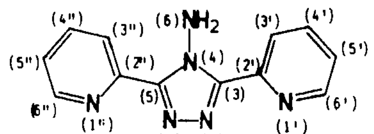
An even more general route for the synthesis of this type of cationic species involves the reaction of solvated $[RhL_2(Me_2CO)_x]ClO_4$ intermediates with the corresponding ligand, in stoichiometric ratio (1:1), giving the compounds $[Rh(NH_2bpt)L_2]ClO_4$ [L_2 = tfb, cod, nbd, (CO)(PPh_3) or $(CO)_2$; (**V**–**IX**)]. Compound **IX** can also be obtained by bubbling carbon monoxide through a dichloromethane solution of any of the $[Rh(NH_2bpt)(diolefin)]ClO_4$ complexes.

Equation (1) can be reversed by adding KOH to the cationic complexes.

Although in all the above mentioned neutral (**I**–**IV**) and cationic (**V**–**IX**) compounds the ligand should be acting as chelate, the atoms involved in coordination are different. Thus, whilst coordination via one pyridine nitrogen and the amine group is proposed for the neutral complexes, the X-ray structure of the cationic $[Rh(NH_2bpt)(CO)_2]^+$ species shows coordination via one pyridine nitrogen and one triazole nitrogen. Therefore, reaction (1) probably implies the initial protonation of the NH group of the coordinated NHbpt anion (six-membered ring) to give the neutral NH_2bpt ligand, followed by a change from a six- to a five-membered ring, according to the higher and well-known stability of the latter rings.

This different coordination is also apparent in the IR spectra of all these complexes. Cationic complexes show, in the 1650–1550 cm^{-1} region, a pattern very similar to that of the free ligand (3 absorption peaks) while neutral complexes show a very different pattern (4 absorption peaks). The ν(CO) band in the related complexes **IV** and **VIII** is in a different posi-

TABLE II. ^1H NMR Data[a] for the Free Ligand and Some Selected Complexes, Numbering Scheme:



Compound	Solvent	T[a] (°C)	$H_{3'}$[b]	$H_{3''}$	$H_{4'}$	$H_{4''}$	$H_{5'}$	$H_{5''}$	$H_{6'}$	$H_{6''}$	H_6	Olefinic H[c] and other H
NH_2bpt[d]	$CDCl_3$	20	8.32dt(2)		7.81td(2)		7.29ddd(2)		8.59ddd(2)		8.43s(2)	
	D_6 acetone	20	8.34dt(2)		8.06td(2)		7.55ddd(2)		8.76ddd(2)		8.40s(1)	
III[e]	$CDCl_3$	20	8.96d(1)	8.42d(1)	7.89t(1)	7.79t(1)	7.13t(1)	7.24t(1)	7.43d(1)	8.56d(1)	9.46s(1)	3.78s(6), 1.41s(2)
IV	$CDCl_3$	20	8.54d(1)	8.24d(1)	7.94t(1)	–	6.88m(1)	–	–	8.66d(1)	9.1s(1)	7.7t(6), 7.35m(9)
VI	D_6 acetone	20	8.58d(2)		8.25td(2)		7.75dd(2)		8.51d(2)		7.47; 7.41(1)	4.79(4), 2.4; 2.16(8)
		–60	8.96d(1)	8.2m(2)*[f]	8.45t(1)	8.16m(1)	7.86t(1)	7.68t(1)	8.2m(2)*	8.78d(1)	7.50; 7.53(1)	4.8(2); 4.55(2) 2.5; 2.1(8)
VII	D_6 acetone	20	8.56m(2)		8.2t(2)		7.74t(2)		8.4m(2)		7.35(1)	4.62(4), 4.16(2), 1.47(2)
		–60	8.96d(1)	8.13m(2)*	8.52t(1)	7.88m(2)**	7.88m(2)**	7.7t(1)	8.13m(2)*	8.8d(1)	7.56(1)	4.6(4), 4.15(2), 1.4(2)
IX	D_6 acetone	20	9.13d(1)	8.31d(1)	8.60td(1)	8.17td(1)	8.02ddd(1)	7.71ddd(1)	9.06d(1)	8.85d(1)	7.47d(1)	
X	$CDCl_3$	20	8.6d(2)		7.98td(2)		7.46ddd(2)		8.32d(2)		8.18s(1)	5.6s(2), 3.9s(4)
XI	$CDCl_3$	20	8.61d(2)		7.98td(2)		7.45ddd(2)		8.3d(2)		8.61s(2)	4.1s(4), 3.9s(2), 1.3s(2)

[a] Spectra were measured at 200 MHz. Chemical shifts are given in δ(ppm) relative to TMS. [b] Accepting that the pyridine group of the ligand coordinated to the Rh atom is that called ('). [c] The diolefin are fluxional in all the cases and they give broad singlets. [d] Coupling constants for the free ligand are: J(H-3, H-4) = 8 Hz, J(H-3, H-5) = 1.2 Hz, J(H-3, H-6) = 1 Hz, J(H-4, H-5) = 7.6 Hz, J(H-4, H-6) = 1.8 Hz and J(H-5, H-6) = 5 Hz. [e] Coupling constants for the complexes are very similar to that of the free ligand. [f] Peaks with the same number of (*) are together (for the same compound). [g] Apparency: s, singlet; d, doublet; t, triplet; m, multiplet; dt, doublet of triplets; td, triplet of doublets, ddd, double doublet of doublets.

tion, being displaced to lower frequencies for the neutral compound.

The ^{1}H NMR spectra of cationic diolefin rhodium complexes described here reveal dynamic behaviour in solution but that by decreasing the temperature of the measurements a slow-exchange limit on the NMR time scale is reached. On the contrary at room temperature the pyridine protons of the ligand of compound **IX** are unequivalent suggesting a rigid coordination of the Rh atom to N(2) and N(1′) atoms.

Addition of stoichiometric amounts (1:1) of HCl to dichloromethane solutions of complexes **I** or **III** results in the formation of red, air stable complexes of formula [RhCl(diolefin)(NH$_2$-bpt)] (diolefin = tfb, nbd) (**X**, **XI**). These compounds can also be prepared by reaction of the corresponding [RhCl(diolefin)]$_2$ with the ligand NH$_2$-bpt.

The IR spectra of **X** and **XI**, in the solid state, do not show the characteristic absorption ν(Rh–Cl) band present in square planar rhodium(I) chlorine complexes [8]; thus, these compounds are probably 'classical' five-coordinated species, but in nitromethane solution they show some conductivity which would suggest an equilibrium between neutral five-coordinated and ionic square-planar species, with ionic Cl$^-$ [9].

The ^{1}H NMR of **X** and **XI** show that, at room temperature, the protons of both pyridines are equivalent according with the usual dynamic behaviour observed in five-coordinated rhodium(I) complexes, and in contrast with the related cationic square-planar complexes.

Addition of AgClO$_4$ to **X** and **XI** leads to the alternative preparation of cationic complexes **V** and **VII** according to eqn. (2)

$$[\mathrm{RhCl(diolefin)(NH_2bpt)}] \xrightarrow[-\mathrm{AgCl}]{+\mathrm{AgClO_4}} [\mathrm{Rh(diolefin)(NH_2bpt)}]\mathrm{ClO_4} \qquad (2)$$

X-Ray Structure of [Rh(CO)$_2$(NH$_2$bpt)]ClO$_4$

The crystals are built up of dimeric units centrosymmetrically related, as shown in Fig.1. Table III displays the main geometrical parameters describing the molecule. The geometry about rhodium is approximately square-planar (see Table III). Distortion arises from the inability of the N(1)–N(11) chelate to achieve a 90° 'bite angle' (N(1)–Rh–N(11) = 78.0(2)°); the angles N–Ni–N of the related [Ni$_2$(NH$_2$bpt)$_2$]$^{4+}$ complex show values of 76.47(4) and 76.94(4)° [5]. The rhodium atoms deviate from the least-square planes of coordination 0.0381(5) Å towards its centrosymmetrical one. The separation between the metal atoms is 3.2386(7) Å, so a weak intermetallic interaction might be present. The related dicarbonyl(2,4-pentanediimine)rhodium(I) cations have been found to form weak dimers with a Rh–Rh distance of 3.271(3) Å, in such a way that these dimers are stacked in a columnar fashion to form a linear alternating rhodium(I) chain [10].

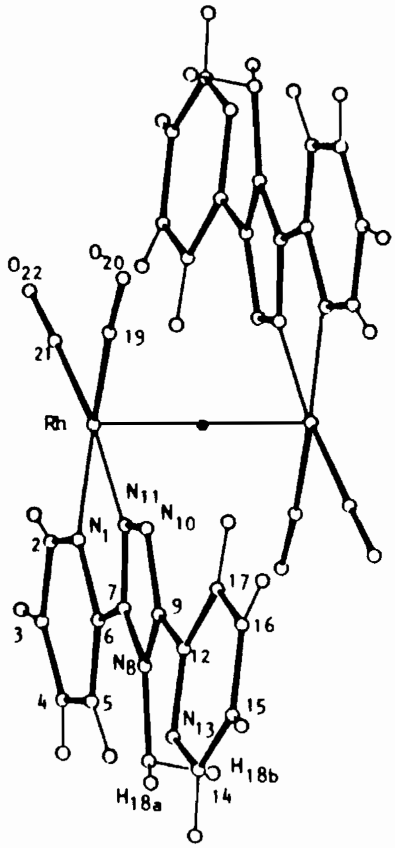


Fig. 1. View of the dimeric units centrosymmetrically related ($i \equiv \bar{x}\,\bar{y}\,\bar{z}$) showing the atomic numbering of complex **IX**. Carbon symbols are omitted for clarity.

The rhodium–ligand distances are within the range normally observed for related rhodium complexes [10–14]. In particular, the rhodium–triazole nitrogen bond [2.033(5) Å] is shorter than the rhodium–pyridine nitrogen bond [2.094(5) Å]. The rings of the NH$_2$bpt ligand are planar with small values of the torsion angles around the C(6)–C(7) and C(9)–C(12) bonds (see Table III). Due to coordination the angle C(6)–C(7)–N(11) [119.3(6)°] is smaller than C(6)–C(7)–N(8) [133.0(6)°]; no difference exists, within precision, for related angles around the atom C(9) due to the lack of implication of that part of the ring in the coordination. However, there is a twist of about 180° around C(9)–C(12) with respect to the [Ni$_2$(NH$_2$btp)$_2$]$^{4+}$ complex [5]. In contrast with the related dicarbonyl (2,4-pentanediimine)rhodium(I) cationic compound [10], no stacking of dimers in a linear fashion is present in the complex reported in this paper.

TABLE III. Main Geometrical Parameters of $[Rh(CO)_2(NH_2bpt)]ClO_4$

(a) Bond distances (A) and angles (°). i: related by the symmetry operation –*x*, –*y*, –*z*; e.s.d.s in parentheses

Rh–Rhi	3.2386(7)	C3–C4	1.348(15)	N11–C7	1.324(7)
Rh–N1	2.094(5)	C4–C5	1.390(12)	N8–N18	1.417(8)
Rh–N11	2.033(5)	C5–C6	1.388(9)	C9–C12	1.471(8)
Rh–C19	1.848(6)	C6–N1	1.363(9)	C12–N13	1.339(8)
Rh–C21	1.864(9)	C6–C7	1.449(8)	N13–C14	1.344(9)
C19–020	1.151(9)	C7–N8	1.355(8)	C14–C15	1.376(10)
C21–022	1.116(13)	N8–C9	1.382(7)	C15–C16	1.373(12)
N1–C2	1.350(11)	C9–N10	1.316(8)	C16–C17	1.380(10)
C2–C3	1.383(13)	N10–N11	1.364(7)	C17–C12	1.392(8)
N1–Rh–C21	96.8(3)	Rh–N1–C2	126.4(6)	C5–C6–C7	126.1(7)
N11–Rh–C19	94.7(2)	Rh–N1–C6	116.0(4)	N11–C7–N8	107.7(5)
C19–Rh–C21	90.5(3)	C2–N1–C6	117.6(6)	N11–C7–C6	119.3(6)
N1–Rh–N11	78.0(2)	Rh–N11–C7	115.3(4)	C6–C7–N8	132.9(5)
N1–Rh–C19	172.6(3)	Rh–N11–N10	134.3(4)	N10–C9–C12	124.5(5)
N11–Rh–C21	173.6(3)	C7–N11–N10	110.4(5)	N10–C9-N8	110.0(5)
Rhi–Rh–C19	89.4(2)	020–C19–Rh	176.2(7)	N8–C9–C12	125.5(5)
Rhi–Rh–C21	100.2(3)	022–C21–Rh	178.5(9)	C9–C12–N13	116.3(5)
N1–Rh–Rhi	90.4(2)	N1–C6–C5	122.5(6)	C9–C12–C17	119.5(6)
N11–Rh–Rhi	83.5(2)	N1–C6–C7	111.4(5)	C9–C12–N13	116.3(5)

(b) Selected torsion angles (°)

C19–Rh–Rhi–C21i	89.6(4)	N1–C6–C7–N8	176.9(6)
C19–Rh–Rhi–N1i	–7.4(3)	C5–C6–C7–N11	–178.8(7)
C19–Rh–Rhi–N11i	–85.2(3)	C5–C6–C7–N8	–1.8(12)
C21–Rh–Rhi–N1i	83.1(3)	N10–C9–C12–N13	165.7(6)
C21–Rh–Rhi–N11i	5.2(3)	C17–C9–C12–N8	164.2(6)
N1–Rh–Rhi–N11i	102.2(2)	N8–C9–C12–N13	–15.0(9)
N1–C6–C7–N11	–0.2(8)	N10–C9–C12–C17	–15.1(9)

(c) Some least-square planes and angles (°) between them

1: Rh, N1, C21   2: Rh, C19, C21   3: Rh, C19, N11   4: Rh, N11, N1   5: N1, C2, C3, C4, C5
6: C7, N8, C9, N10, N11

1–2 178.9(2)   1–3 3.8(2)   1–4 3.6(2)   2–3 176.4(2)   2–4 176.4(2)   3–4 0.7(2)
5–6 4.4(3)

(d) Geometry of the hydrogen interactions. Distances (A) and angles (°).

N13······H18a	2.21(6)	N13···N18	2.838(8)	N18–H18a	0.78(6)
O1·······H18b	2.20(11)	O1····N18	3.122(17)	N18–H18b	0.99(11)
O4·······H18b	2.46(10)	O4····N18	3.244(17)	C16–H16	1.00(7)
O1(vi)····H16	2.48(7)	C16··O1(vi)	3.295(14)		

N18–H18a···N13	138(6)	N18–H18b···O4	135(7)
N18–H18b···O1	155(8)	C16–H16 ····O1(vi)	138(6)

There are two short contacts, N(18)–H(18a)··· N(13) and N(18)–H(18b)···O(1) (of the ClO_4^- anion), which have a geometry indicative of hydrogen bonds [15], plus two longer interactions [N(18)–H(18b)···O(4) and C(16)–H(16)···O(1)vi*] (see Table III).

Experimental

Reactions were carried out in air (except when $L_2 = (CO)_2$). The solvents were dried by standard methods and distilled before use. C, H and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. Conductivities were measured at 20 °C in *ca.* 5×10^{-4} M acetone or nitromethane solutions using a 9501/01 conductimeter. IR spectra were recorded on a Perkin-Elmer 599 spectro-

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*vi: symmetry operation –*x*, 1 – *y*, 1 – *z*.

photometer over the range of 4000–200 cm^{-1}, using Nujol mulls between polyethylene sheets or in dichloromethane solutions between NaCl plates. NMR spectra were recorded on a Varian XL 200 Spectrometer.

Synthesis of Complexes I–IV

To a solution of 'K(NHbpt)' (prepared by treating NH_2bpt (48 mg, 0.2 mmol) with KOH in methanol (0.1 N) (0.22 mmol, 2.2 ml) in dichloromethane (3 ml)) was added $[RhCl(L_2)]_2$ (L_2 = tfb, cod, nbd or CO-PPh_3) (0.1 mmol) and diethylether (15 ml). The mixture was stirred for 3 h at room temperature; orange solids appeared which were filtered, washed with diethylether and vacuum dried. The solids were purified by dissolving them in dichloromethane (3 ml), filtering the solution and removing the solvent under vacuum.

When L_2 = (CO)(PPh_3) the reaction is carried out in a mixture of dichloromethane–hexane (1:5) because complex **IV** is quite soluble in diethylether.

Complex [Rh(tfb)(NHbpt)] (**I**) is obtained in almost quantitative yield when methanol is used as solvent instead of dichloromethane. The complex is not soluble in methanol and it precipitates as it is formed, so the KCl remains in the methanolic solution, and further purification is not necessary.

Synthesis of Complexes V–IX

Method A. To a suspension of $[Rh(L_2)(NHbpt)]$ (L_2 = tfb, cod, nbd or (CO)(PPh_3); complexes **I–IV**) (0.1 mmol) in acetone (5 ml) was added $HClO_4$ (0.1 mmol). Evaporation of the solutions to *ca.* 1 ml and addition of diethylether (15 ml) gave complexes **V–VIII** as microcrystalline solids which were filtered off, washed with diethylether and then dried *in vacuo*.

Method B. An acetone solution (15 ml) of $[Rh(L_2)(OCMe_2)_x]^+$ (L_2 = tfb, cod, nbd, (CO)(PPh_3) or $(CO)_2$) (prepared by treating the appropriate $[RhClL_2]_2$ (0.1 mmol) with $AgClO_4$ (42 mg, 0.2 mmol) in acetone for 30 min and filtering off the AgCl formed) was added to a solution of NH_2bpt (48 mg, 0.2 mmol) in acetone. Evaporation of the solution to *ca.* 1 ml and addition of diethylether (15 ml) gave complexes **V–IX** as microcrystalline solids which were filtered off, washed with diethylether and then dried *in vacuo.*

An alternative route for preparation of complex **IX**, $[Rh(CO)_2(NH_2bpt)]ClO_4$, is the diolefin displacement by CO in complexes **V–VII**. Dry carbon monoxide was bubbled through a dichloromethane solution (5 ml) of complexes $[Rh(diolefin)(NH_2bpt)]ClO_4$ (diolefin = tfb, cod, nbd) (0.1 mmol) for 15 min. The orange colour of the initial solution turned to dark green and a dark green solid of complex $[Rh(CO)_2(NH_2bpt)]ClO_4$ precipitated.

Syntheses of Complexes X and XI

Method A. To a dichloromethane (5 ml) solution of complexes **I** or **III** (0.10 mmol) was added HCl (0.1 mmol). Stirring for 30 min afforded red solids which were filtered, washed with diethyl ether and vacuum dried.

Method B. To a dichloromethane (5 ml) suspension of NH_2bpt (0.30 mmol) was added $[RhCl(diolefin)]_2$ (0.15 mmol). Stirring for 1 h afforded red solids which were filtered, washed with diethylether and vacuum dried.

Determination and Refinement of the Structure

Crystal data are listed in Table IV. The stability and orientation of the crystal were checked each 90

TABLE IV. Crystal Data and Data Collection Parameters of Compound **IX**.

Crystal data	
Formula	$C_{14}H_{10}N_6O_2RhClO_4$
Crystal habit	Prismatic rectangular base
Crystal size (mm)	0.33 × 0.13 × 0.03
Symmetry	monoclinic, $P2_1/n$
Unit cell determination	Least-squares fit from 85 reflexions ($\theta < 45°$)
Unit cell dimensions	17.6130(6), 11.3072(2), 9.0013(2) A $\beta = 101.536(2)°$
Packing: V (A^3), Z	1756.43(8), 4
D_c (g cm^{-3}), M, $F(000)$	1.878, 496.63, 984
μ (cm^{-1})	99.2
Experimental data	
Technique	four circle diffractometer bisecting geometry graphite oriented monochromator, Cu Kα $\omega/2\theta$ scans, scan width: 1.5
Total measurements	up to 65°
Number of reflexions	
Measured	2993
Independent	2993
Observed	2479 ($3\sigma(I)$ criterion)
Max–min. transmission factors	1.161 0.755
Solution and refinement	
Solution	Patterson function and DIRDIF
Refinement	L.S. on Fobs with 1 block
H atoms	Difference synthesis
Final F peaks	0.82 e/A^3 in a centre of symmetry
Final R and R_w	0.049–0.058
Computer and programs	VAX 11/750 XRAY76 System [16], DIRDIF [17]
Scattering factors	Int. Tables for X-Ray Crystallography [18].

min with two reference reflections. No significant variations in the diffracted intensities were detected during data collection. An empirical absorption correction was applied [19]. A weighting scheme was used as to give no trends in $\langle w^2F \rangle$ *vs.* $\langle F_o \rangle$ or $\sin \theta/\lambda$. No extinction correction was found necessary.

The final positional parameters are given in Table V for non-hydrogen atoms.

TABLE V. Final Atomic Coordinates

Atom	*x/a*	*y/b*	*z/c*
Rh	0.02949(3)	0.07249(4)	−0.13294(5)
N1	−0.0851(3)	0.1164(5)	−0.2309(6)
C2	−0.1305(5)	0.0618(10)	−0.3496(10)
C3	−0.2055(5)	0.0982(10)	−0.4079(10)
C4	−0.2356(5)	0.1897(10)	−0.3428(10)
C5	−0.1912(4)	0.2487(8)	−0.2201(9)
C6	−0.1159(4)	0.2098(6)	−0.1677(7)
C7	−0.0599(3)	0.2617(5)	−0.0450(7)
N8	−0.0623(3)	0.3567(5)	0.0456(6)
C9	0.0107(3)	0.3655(6)	0.1364(7)
N10	0.0554(3)	0.2802(5)	0.1034(6)
N11	0.0106(3)	0.2159(5)	−0.0092(6)
C12	0.0353(3)	0.4556(5)	0.2541(7)
N13	−0.0109(3)	0.5500(5)	0.2502(7)
C14	0.0103(5)	0.6310(7)	0.3599(9)
C15	0.0763(5)	0.6205(7)	0.4705(9)
C16	0.1234(4)	0.5235(7)	0.4721(8)
C17	0.1031(4)	0.4383(6)	0.3617(7)
N18	−0.1278(3)	0.4306(7)	0.0410(8)
C19	0.1307(4)	0.0512(6)	−0.0318(8)
O20	0.1924(3)	0.0393(6)	0.0387(8)
C21	0.0398(5)	−0.0510(8)	−0.2647(10)
O22	0.0463(5)	−0.1233(8)	−0.3455(10)
Cl	−0.2857(1)	0.2757(2)	0.1735(2)
O1	−0.2522(9)	0.3800(14)	0.2359(13)
O2	−0.3190(5)	0.2112(10)	0.2753(10)
O3	−0.3432(8)	0.3088(10)	0.0511(12)
O4	−0.2324(8)	0.2110(13)	0.1166(16)

Supplementary Material

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

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