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The crystal and molecular structure of bis(indazol-1-yl)pyridin-2′-ylmethane (BIPM) and [Rh(BIPM)(NBD)]PF_6

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Abstract

The syntheses of a new tripodal ligand bis(indazol-1-yl)pyridin-2′-ylmethane (BIPM) and of a cationic complex [Rh(BIPM)(NBD)]PF_6, (NBD = 2,5-norbornadiene) are reported. Both compounds were characterized by infrared, ^1H, and ^{13}C NMR spectroscopy and by single crystal X-ray analysis. BIPM crystallizes in the monoclinic system in space group $P2_1/n$ with an $\alpha\beta\alpha$ helical conformation. The [Rh(BIPM)(NBD)]PF_6 complex crystallizes in the monoclinic space group $C/2c$, the rhodium atom being pentacoordinate with a distorted trigonal bipyramidal geometry.

1. Introduction

Polydentate ligands able to form stable complexes with most transition metal ions have been the focus of much attention in recent years, both in analytical and coordination chemistry [1–3]. Even when a potentially tridentate ligand (NNN) is present, coordination may occur through only one or two of the donor atoms. It might be possible to prepare rhodium complexes with such ligands and use them for catalytic reactions. Most mixed-ring chelating ligands contain azoles and pyridines. Among the tripodal nitrogen ligands tris(pyrazol-1-yl)methane [4] and the isoelectronic tris(pyrazol-1-yl)borate anion [2,5], the terpyridine types in which one, two or three pyridine rings are replaced by pyrazole rings [6], tris(pyridin-2-yl)methane [7] and bis(pyrazol-1-yl)pyridin-2′-ylmethane [8] or bis(pyrazol-1-yl)*N*-methylimidazol-2′-ylmethane [8] received special attention.

We report here the synthesis and characterization of a related tripod ligand, bis(indazol-1-yl)pyridin-2′-ylmethane (BIPM) (1) containing an unsymmetrical donor set, and its reactivity towards the dimeric complex [{Rh(NBD)Cl}$_2$] (NBD = 2,5-norbornadiene or bicyclo[2.2.1]hepta-2,5-diene). The X-ray crystal structures of the cationic complex [Rh(BIPM)(NBD)]PF_6 (2) and of the free BIPM (1) are also discussed.

2. Experimental details

Melting points were determined on a hot stage microscope and are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 298 K on Bruker AC-200

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(200.13 and 50.33 MHz) and Bruker AM-360 (360.13 and 90.55 MHz) spectrometers. Chemical shifts are in ppm relative to tetramethylsilane and coupling constants are in Hz. The ^1H and ^{13}C chemical shifts are accurate to 0.01 and 0.1 ppm, respectively. Coupling constants are accurate to ±0.2 Hz for ^1H NMR spectra and ±0.6 Hz for the ^{13}C NMR spectra. Homonuclear ^1H-^1H COSY-45 was performed in the usual manner [9]. IR spectra were recorded on a IBM-PU-9512 spectrometer and the conductivity measured at 20°C with a Philips PW 9526 conductometer. Mass spectra were determined on a VG-12-250 spectrometer at 70 eV. Column chromatography was carried out through silica gel Merck 60 (70–230 mesh). Indazole and pyridine-2-carboxaldehyde were purchased from commercial sources and used without further purification. Zinc chloride was stored in a vacuum desiccator prior to use.

2.1. Preparation of bis(indazol-1-yl)pyridin-2'-ylmethane (1)

A round-bottomed flask was fitted with a reflux condenser attached to a drying tube ($CaCl_2$) and with magnetic stirrer. The flask was charged with indazole (2 g, 16.9 mmol), pyridine-2-carboxaldehyde (0.904 g, 8.45 mmol) and $ZnCl_2$ (58 mg, 0.42 mmol). The mixture was heated with stirring on an oil bath at 120°C for 17 h. After cooling to room temperature, the reaction mixture was purified by chromatography on a silica gel column with chloroform/ethyl acetate 95/5 as the eluting solvent. Recrystallization from ethanol afforded pure **1** (660 mg, 24%), mp 157–158°C. Anal. Found: C, 73.62; H, 4.74; N, 21.64% $C_{20}H_{15}N_5$ (M_r = 325.37) calcd.: C, 73.83; H, 4.65; N, 21.52%. Mass spectrum: M^+ = 325. IR (KBr): 3070, 2940, 1600, 1580, 1490, 1460, 1410, 1330, 1290, 1225, 1200, 1170, 1120, 1010, 900, 830, 750 cm^{-1}.

2.2. Preparation of [Rh(BIPM)(NBD)]PF_6 (2)

To a suspension of [{RhCl(NBD)}$_2$] (100.8 mg, 0.22 mmol) in 30 ml of methanol bis(indazol-1-yl)pyridin-2'-ylmethane (1) (139 mg, 0.43 mmol) was added. The reaction mixture was vigorously stirred for 45 min, the initial suspension becoming transparent deep yellow solution. The addition of KPF_6 (90 mg, 0.49 mmol) instantly afforded a yellow microcrystalline solid which was filtered off and dried under vacuum. The compound was recrystallized in methanol to give 135 mg of the complex **2** (47%). Anal. Found: C, 48.50; H, 3.90; N, 10.30% $C_{27}H_{23}F_6N_5PRh \cdot 1/4H_2O$ (M_r = 669.89)

TABLE 1. Crystal and refinement data for (BIPM) (**1**) and [Rh(BIPM)(NBD)]PF_6 (**2**)

	1	**2**
Formula	$C_{20}N_5H_{15}$	$C_{27}H_{23}F_6N_5PRh$
M_r	325.37	665.36
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$
a (Å)	10.459 (1)	28.85 (2)
b (Å)	12.279 (2)	10.761 (2)
c (Å)	13.049 (3)	25.501 (2)
β (°)	102.20 (1)	135.57 (4)
V (Å^3)	1638.0 (5)	5542 (6)
Z	4	8
F(000)	680	2672
ρ (calcd) (g cm^{-3})	1.32	1.64
temp (K)	294	294
μ (cm^{-1})	0.77	7.32
Cryst. dimension (mm)	0.25 × 0.2 × 0.15	0.3 × 0.4 × 0.2
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation	Graphite-monochromated Mo Kα (λ = 0.71069 Å)	Graphite-monochromated Mo Kα (λ = 0.71069 Å)
Scan technique	$\omega/2\theta$	$\omega/2\theta$
Data collected	(−12, 0, 0) to (12, 14, 15)	(−34, 0, 0) to (34, 12, 30)
θ	$1 < \theta < 25$	$1 < \theta < 25$
Unique data	2870	4866
Unique data (I) ≥ 2σ (I)	2093	3250
R(int.) (%)	1.0	1.8
R_F (%)	4.0	5.8
R_{wF} (%)	4.1	5.9
Average shift/error	0.18	0.6

calcd.: C, 48.41; H, 3.54; N, 10.45%. IR (KBr): 3580 and 3630 (OH), 3140 and 3000 (CH, NBD), 840 and 760 (PF_6^-) cm^{-1}. Molar conductivity $\Lambda = 65 \times 10^{-4}$ S m^2 mol^{-1} (6×10^{-4} mol dm^{-3} solution of **2** in nitromethane).

2.3. *X-ray structure determination*

Single colourless prismatic crystals of **1** and yellow octahedral crystals of **2** were obtained from ethanol and methanol, respectively. The data were collected with an Enraf-Nonius CAD-4F diffractometer for both compounds and unit cell constants were refined from leastsquares fitting of the setting angles of 25 reflections. Three standard reflections measured at intervals shared no significant variation. A summary of the fundamental crystal data is given in Table 1.

The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Rh and P were taken from the *International Tables for X-ray Crystallography* [10]. Both structures were solved by MULTAN and Fourier methods using the X-RAY 80 system [11]. Empirical absorption corrections [12] were applied at the end of the isotropic refinements.

For **1**, mixed full-matrix least-squares refinement with unit weights and fixed temperature factors for H atoms led to $R = 4.0$ and $R_w = 4.1$.

TABLE 2. Atomic coordinates and thermal parameters as $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j \times 10^4$ for non-hydrogen atoms of **1**

Atom	x	y	c	U_{eq}
N1	0.5407(2)	0.4992(2)	0.3492(2)	528(8)
N2	0.5404(2)	0.3887(1)	0.3480(1)	428(6)
N3	0.3580(2)	0.2927(1)	0.3875(1)	430(7)
N4	0.3371(2)	0.1990(2)	0.3295(2)	504(7)
N5	0.7086(2)	0.2673(2)	0.4904(2)	617(8)
C1	0.4889(2)	0.3322(2)	0.4283(2)	420(8)
C2	0.5824(2)	0.2453(2)	0.4837(2)	439(8)
C3	0.5400(3)	0.1561(2)	0.5302(2)	573(10)
C4	0.6317(3)	0.0846(2)	0.5854(2)	677(12)
C5	0.7616(3)	0.1049(3)	0.5922(2)	680(12)
C6	0.7956(3)	0.1960(3)	0.5448(3)	737(12)
C7	0.5884(3)	0.5278(2)	0.2672(3)	652(11)
C8	0.6194(2)	0.4381(2)	0.2116(2)	539(9)
C9	0.6696(3)	0.4218(3)	0.1201(2)	778(14)
C10	0.6842(3)	0.3187(3)	0.0891(3)	812(14)
C11	0.6515(3)	0.2294(3)	0.1430(2)	668(11)
C12	0.6033(3)	0.2419(2)	0.2327(2)	547(10)
C13	0.5874(2)	0.3480(2)	0.2650(2)	430(8)
C14	0.2111(3)	0.1967(2)	0.2899(2)	546(10)
C15	0.1459(2)	0.2897(2)	0.3178(2)	501(9)
C16	0.0169(3)	0.3292(3)	0.2990(3)	708(12)
C17	−0.0061(3)	0.4273(3)	0.3394(3)	814(14)
C18	0.0955(3)	0.4899(3)	0.3984(3)	687(12)
C19	0.2218(2)	0.4533(2)	0.4191(2)	534(9)
C20	0.2445(2)	0.3520(2)	0.3789(2)	415(8)

TABLE 3. Atomic coordinates and thermal parameters as $U_{eq} = 1/3\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j \times 10^3$ for non-hydrogen atoms of **2**

Atom	x	y	z	U_{eq}
Rh	0.1443(0)	0.1210(1)	0.2149(0)	22(2)
N1	0.0547(3)	0.0864(6)	0.1863(3)	48(5)
N2	0.0316(3)	−0.0328(6)	0.1713(4)	50(5)
N3	0.1321(3)	−0.1485(6)	0.2481(3)	52(5)
N4	0.1777(3)	−0.0581(7)	0.2789(4)	52(5)
N5	0.1003(3)	−0.0069(7)	0.1238(4)	57(6)
C1	0.0667(4)	−0.1307(8)	0.1726(4)	52(6)
C2	0.0708(4)	−0.1104(9)	0.1175(4)	52(6)
C3	0.0465(5)	−0.1994(9)	0.0636(5)	69(8)
C4	0.0512(6)	−0.1811(11)	0.0144(5)	85(9)
C5	0.0803(6)	−0.0762(12)	0.0204(5)	80(9)
C6	0.1042(5)	0.0115(10)	0.0748(5)	69(8)
C7	0.0119(4)	0.1568(7)	0.1770(4)	50(6)
C8	−0.0405(4)	0.0849(8)	0.1552(4)	49(6)
C9	−0.0981(4)	0.1115(10)	0.1369(5)	64(7)
C10	−0.1380(5)	0.0144(12)	0.1175(5)	77(9)
C11	−0.1224(5)	−0.1078(10)	0.1158(5)	70(8)
C12	−0.0674(4)	−0.1375(8)	0.1326(4)	57(6)
C13	−0.0258(4)	−0.0369(7)	0.1524(4)	45(6)
C14	0.2330(4)	−0.0986(8)	0.3459(4)	55(6)
C15	0.2220(4)	−0.2170(8)	0.3596(4)	55(7)
C16	0.2607(5)	−0.3015(10)	0.4203(5)	78(8)
C17	0.2309(6)	−0.4062(10)	0.4133(6)	89(10)
C18	0.1649(6)	−0.4334(9)	0.3486(6)	83(10)
C19	0.1263(5)	−0.3565(8)	0.2883(5)	67(8)
C20	0.1568(4)	−0.2483(8)	0.2957(4)	51(7)
C21	0.2060(5)	0.2177(9)	0.2130(6)	69(9)
C22	0.1491(7)	0.2866(14)	0.1727(7)	115(13)
C23	0.1529(8)	0.3662(14)	0.2183(9)	134(17)
C24	0.1618(6)	0.2842(10)	0.2725(7)	73(10)
C25	0.2222(8)	0.2373(17)	0.3134(7)	131(14)
C26	0.2501(6)	0.2656(20)	0.2894(8)	144(13)
C27	0.2281(6)	0.4099(10)	0.2723(7)	88(12)
P	0.4243(2)	0.0102(3)	0.0517(2)	104(3)
F1	0.3789(13)	0.0725(27)	0.0574(13)	195(0)
F2	0.4815(8)	0.0962(15)	0.1183(9)	120(0)
F3	0.4035(8)	0.1360(16)	0.0019(9)	128(0)
F4	0.4759(10)	−0.0126(21)	0.0406(12)	178(0)
F5	0.3709(9)	−0.0728(19)	−0.0162(11)	155(0)
F6	0.4510(12)	−0.1035(26)	0.0939(13)	196(0)
F21	0.4584(12)	0.1328(24)	0.0647(14)	191(0)
F22	0.3585(7)	0.0522(16)	0.0252(7)	103(0)
F23	0.3891(7)	−0.0159(14)	−0.0298(8)	103(0)
F24	0.4862(7)	−0.0693(14)	0.0870(8)	109(0)
F25	0.4543(8)	0.0401(16)	0.1351(9)	134(0)
F26	0.4038(11)	−0.1199(22)	0.0623(13)	173(0)

In complex **2**, the fluorine atoms of the $[PF_6]^-$ were located in a F in difference map disorder over 12 positions, and consequently these atoms were only refined isotropically with a population factor of 0.5. Final mixed refinement with fixed isotropic factors and coordinates for H atoms, except for H1(C1) for which coordinates were refined, converged at $R = 5.8$ and $R = 5.9$.

Refined atomic coordinates for **1** and **2** are given in Table 2 and Table 3, respectively.

3. Results and discussion

3.1. Syntheses

Bis(indazol-1-yl)pyridin-2′-ylmethane (BIPM) was prepared in one step from indazole and pyridine-2-carboxaldehyde in the presence of a catalytic amount of zinc chloride [13,14] (Scheme 1). This procedure was more convenient than the alternative involving pyridine-2-carboxaldehyde ethylene acetal [15].

The reaction of the dinuclear complex [{RhCl-(NBD)}$_2$] with BIPM (**1**) in a 1:2 molar ratio in methanol yielded a stable yellow solid when KPF_6 was added to the reaction solution. The complex isolated was characterized by elemental C, H, and N analyses, Infrared, ^1H and ^{13}C NMR spectroscopy and conductivity measurements as the hexafluorophosphate salt [Rh(BIPM)(NBD)]PF_6 (**2**). When the tripodal tris(pyrazol-1-yl)methane (TPzM) was employed in a similar reaction (1:2 molar ratio) [4a], the neutral halide complex [RhCl(NBD)(TPzM)] was isolated as a precipitate from the reaction solution. A cationic complex was obtained only in an ion pair [Rh(NBD)-(TPzM)]$^+$[$RhCl_2$(NBD)]$^-$ if the reaction was carried out in a 1:1 molar ratio. This suggests that cationic species of type [Rh(NBD)(NNN)]$^+$ are stabilized when the tripodal NNN ligand is bis(indazol-1-yl)pyridin-2′-ylmethane (BIPM) rather than tris(pyrazol-1-yl)-methane. Thus there is a greater tendency for cationic five-coordination in rhodium(I) species with BIPM, which is certainly related to the steric and electronic characteristics of this new mixed system. The crystal structure of the complex (see later) proves the five coordination.

3.2. NMR analysis

The ^1H NMR data of ligand BIPM were obtained in $CDCl_3$ and CD_3OD solutions (Table 4). All protons were unequivocally assigned in both solvents from the characteristic coupling patterns by comparison with the spectra of other analogues [13,14]. However, there are some differences.

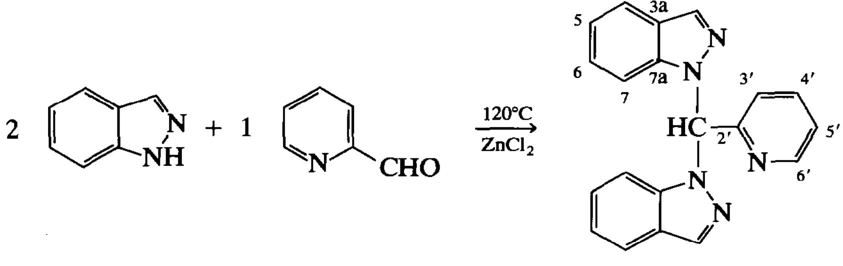
(i) A downfield shift (0.13 ppm) of the C–H proton, which resonates at even lower field than proton $H_{6'}$, is observed in CD_3OD.

(ii) Protons H_4, H_5, H_6, H_7, $H_{3'}$, $H_{4'}$ and $H_{5'}$ resonate in a narrower range of frequencies in $CDCl_3$ than in CD_3OD.

In this solvent each proton, (except $H_{3'}$ which resonates at the same frequency as H_5) could be individually identified. It was therefore possible to observe and measure for $H_{5'}$ a long-range coupling constant ($^6J = 0.61$ Hz) with the C–H proton, confirmed by decoupling experiments. This type of long-range coupling was previously observed in 1-[(5-nitro-2-furfurylidene)-amino]pyrazole [16].

^{13}C NMR spectra were obtained in $CDCl_3$ (Table 5). All carbon atom resonances were completely assigned and the chemical shift of C_3 ($\delta = 134.9$ ppm) is consistent with those previously found for indazole 1-substituted [17].

^1H NMR chemical shifts, coupling constants and coordination induced shifts (CIS $= \delta_{\text{complex}} - \delta_{\text{ligand}}$) of [Rh(BIPM)(NBD)]$PF_6$ in $CDCl_3$ and CD_3OD are shown in Table 4. Important changes in chemical shifts were observed in $CDCl_3$, and assignment of the protons was made by homonuclear two-dimensional correlation (COSY-45). Coordination to rhodium produces a strong deshielding of H_7 and $H_{3'}$ (CIS $= +1.10$ and $+1.45$). This deshielding is produced mainly by Van der Waals effect and σ-donation contributions, as has been previously postulated for a bipyridineruthenium complex [18]. Protons H_3, H_5, H_6, CH, $H_{4'}$ and $H_{5'}$ undergo a milder deshielding (CIS values $+0.12$ to $+0.26$). Only H_4 and $H_{6'}$ have a small negative CIS (-0.03 and -0.04), as a consequence of metal-to-ligand π-donation and through-space ring-current anisotropy effects [19,20]. The latter effect, which has been described for protons adjacent to co-ordinating nitrogen atoms, only appears in our complex in the pyridine ring, but not in the indazole ring, and H_3 has a positive CIS ($+0.24$). Therefore, other deshielding effects are operative.



1 (24%)

Scheme 1.

TABLE 4. ^{1}H NMR data of bis(indazol-1-yl)pyridin-2'-ylmethane (BIPM) (1) and [Rh(BIPM)(NBD)]PF$_6$ (2). Coordination induced shifts (CIS) are in parentheses

Solvent	H_3	H_4	H_5	H_6	H_7	CH	$H_{3'}$	$H_{4'}$	$H_{5'}$	$H_{6'}$	NBD-protons
$CDCl_3$											
	BIPM [a]										
	8.10(d)	7.71(ddd)	7.14(ddd)	7.31(ddd)	7.50(dddd)	8.46(s)	7.23–7.35(m)	7.70(ddd)	7.23–7.35(m)	8.64(ddd)	
	$J_{37}=0.8$; $J_{45}=8.0$; $J_{46}=1.1$; $J_{47}=1.0$; $J_{56}=7.0$; $J_{57}=1.0$; $J_{67}=8.4$; $J_{3'4'}=0.9$; $J_{4'5'}=7.7$; $J_{4'6'}=1.8$; $J_{5'6'}=4.8$										
	[Rh(BIPM)(NBD)]PF$_6$ [b,c]										
	8.34(s)	7.68(d)	7.26 [d]	7.69 [e]	8.60(m)	8.72(s)	8.74(m)	7.95(ddd)	7.44(ddd)	8.60(m)	CH_2-7: 1.45(t), $J=1.6$ CH-2, 3, 5, 6: 3.54(dd); $J=5.0$, 2.2 CH-1, 4: 3.96(bs)
	(+0.24)	(−0.03)	(+0.12)	(+0.38)	(+1.10)	(+0.26)	(+1.45)	(+0.25)	(+0.15)	(−0.04)	
CD_3OD											
	BIPM [a]										
	8.10(d)	7.75(ddd)	7.16(ddd)	7.33(ddd)	7.50(dddd)	8.59(s)	7.18 [f]	7.83(ddd)	7.43(dddd)	8.54(ddd)	
	$J_{37}=0.9$; $J_{45}=8.0$; $J_{46}=1.1$; $J_{47}=1.0$; $J_{56}=6.9$; $J_{57}=0.9$; $J_{67}=8.5$; $J_{4'3'}=7.7$; $J_{3'6'}=0.9$; $J_{4'5'}=7.7$; $J_{4'6'}=1.8$; $J_{5'6'}=4.9$; $J_{5'CH}=0.6$										
	[Rh(BIPM)(NBD)]PF$_6$ [a,b]										
	9.22(s)	8.33(ddd)	7.98(ddd)	8.07–8.19(m)	8.71(cd)	9.10(s)	8.07–8.19(m)	8.58(ddd)	8.07–8.19(m)	9.38(cd)	CH_2-7: 1.40(t), $J=1.6$ CH-2, 3, 5, 6: 3.71(dd); $J=5.0$, 2.2 CH-1, 4: 4.03(bs)
	$J_{45}=8.0$; $J_{46}=1.0$; $J_{47}=1.0$; $J_{56}=7.0$; $J_{67}=8.7$; $J_{3'4'}=7.8$; $J_{4'5'}=7.8$; $J_{4'6'}=1.6$										
	(+1.12)	(+0.58)	(+0.82)	(+0.8)	(+1.21)	(+0.51)	(+0.95)	(+0.75)	(+0.70)	(+0.84)	

Apparent multiplicity is given on the table: s = singlet, d = doublet, cd = complex doublet, m = multiplet, t = triplet, bs = broad signal. [a] At 200 MHz. [b] Very slow solubility. [c] Assignation by COSY at 360.13 MHz. [d] Masked by $CDCl_3$ [e] Masked by H_4. [f] Masked by H_5.

TABLE 5. ^{13}C NMR data of bis(indazol-1-yl)pyridin-2'-ylmethane (BIPM) (1) and [Rh(BIPM)(NBD)]PF$_6$ (2) in $CDCl_3$. Coordination induced shifts (CIS) are in parentheses

Compound	C_3	C_{3a}	C_4	C_5	C_6	C_7	C_{7a}	CH	$C_{2'}$	$C_{3'}$	$C_{4'}$	$C_{5'}$	$C_{6'}$	NBD-carbons
BIPM [a]	134.9	124.7	121.5	121.0	126.9	110.2	139.9	75.4	154.4	122.6	136.9	123.6	149.6	
	$^1J=189.3$		$^1J=160.8$	$^1J=161.6$	$^1J=160.9$	$^1J=165.6$		$^1J=148.2$		$^1J=168.1$	$^1J=162.7$		$^1J=180.1$	
[Rh(BIPM)(NBD)]PF$_6$ [b]	137.0	125.8	123.8	120.6	130.6	110.3	140.7	66.7	150.8	122.7	139.7	127.0	150.1	$C_{1,4}$: 59.0; $J_{Rh}=6.6$ $C_{2,3,5,6}$: 41.4; $J_{Rh}=13.0$ C_7: 47.9; $J_{Rh}=2.7$
	(+2.1)	(+1.1)	(+2.3)	(−0.4)	(+3.7)	(+0.1)	(+0.8)	(−8.7)	(−3.6)	(+0.1)	(+2.8)	(+3.4)	(+0.5)	

[a] At 50.33 MHz. [b] At 90.55 MHz.

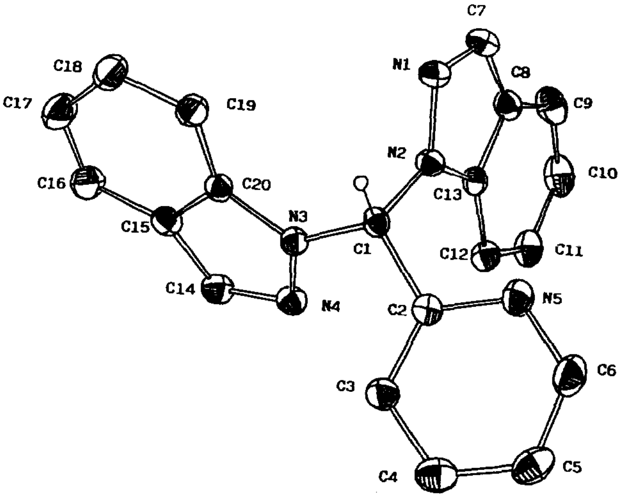


Fig. 1. Structure and numbering scheme of bis(indazol-1-yl) pyridin-2'-ylmethane (BIPM) (1).

Data obtained in CD_3OD reveal a strong solvent effect and only positive CIS (+1.21 to +0.58) were observed. This was also found in related tris(pyrazol-1-yl)methanerhodium complexes [4].

These results show that there are difficulties in the assessment and rationalisation of the behaviour of the complexes in solution by proton NMR spectroscopy. As claimed by other authors [20], a combination of many factors must be taken into account if the sign and magnitude of the observed CIS values are to be rationalized.

The NBD proton resonance were clearly identified by their coupling patterns. No significant chemical shift changes were observed in either solvents.

^{13}C NMR CIS values in $CDCl_3$ (Table 2) cover a broad range (+3.7 to −8.7 ppm) but do not correlate in sign or magnitude with ^1H values in the solvent. This is common in other complexes [20]. The most affected carbon atom is the methane CH (CIS = −8.7) as observed for other tris(pyrazolyl)rhodium complexes [4]. NBD carbon atoms were easily recognized by their rhodium coupling constants. In contrast to other NBD–rhodium complexes [21], the most shielded carbons are olefinic, with $\delta = 41.1$ ppm and $J_{Rh} = 13.0$ Hz.

3.3. Crystal structures of (BIPM) and [Rh(BIPM)(NBD)]PF_6

Figure 1 shows an ORTEP [22] perspective of bis(indazol-1-yl)pyridin-2'-ylmethane, including the atom numbering scheme. The bond, distances and angles are in Table 6.

The helical conformation of the BIPM ligand can be defined by the angles between the mean plane through the pyrazole or pyridine rings and that defined by C1, H1 and the first atom (N2, N3 and C2) of each ring. As can be seen from Table 7, the values [23] of these angles are comparable with those observed for tris(3,5-dimethylpyrazol-1-yl)methane [24], considering the asymmetry introduced by the pyridine ring. All the indazole and pyridine rings are planar within experimental error.

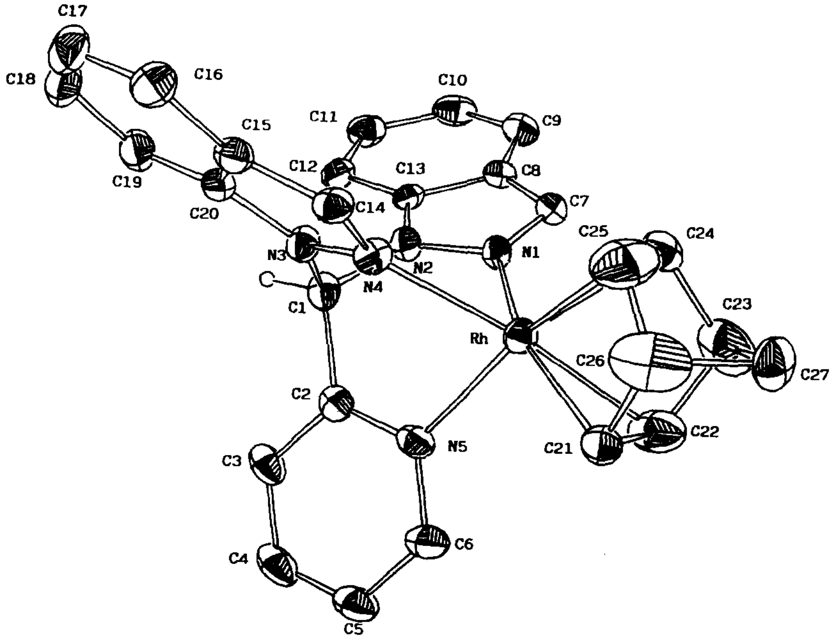


Fig. 2. Structure and numbering scheme of [Rh(BIPM)(NBD)]PF6 (2).

TABLE 6. Bond distances (Å) and angles (°) for 1

N1–N2	1.357(3)	C7–C8	1.394(4)
N1–C7	1.320(4)	C8–C9	1.416(4)
N2–C1	1.452(3)	C8–C13	1.386(4)
N2–C13	1.375(3)	C9–C10	1.348(6)
N3–N4	1.369(3)	C10–C11	1.384(5)
N3–C1	1.444(3)	C11–C12	1.377(4)
N3–C20	1.377(3)	C12–C13	1.390(4)
N4–C14	1310(3)	C14–C15	1.417(4)
N5–C2	1.332(3)	C15–C16	1.406(4)
N5–C6	1.352(4)	C15–C20	1.392(3)
C1–C2	1.524(3)	C16–C17	1.357(5)
C2–C3	1.370(4)	C17–C18	1.403(4)
C3–C4	1.385(4)	C18–C19	1.367(4)
C4–C5	1.366(5)	C19–C20	1.390(4)
C5–C6	1.361(5)	H1–C1	1.01(3)
N2–N1–C7	105.9(2)	N1–C7–C8	112.4(3)
N1–N2–C13	111.9(2)	C7–C8–C13	105.2(2)
N1–N2–C1	118.0(2)	C7–C8–C9	135.9(3)
C1–N2–C13	130.1(2)	C9–C8–C13	118.9(3)
C1–N3–C20	125.9(2)	C8–C9–C10	118.1(3)
N4–N3–C20	111.4(2)	C9–C10–C11	122.4(3)
N4–N3–C1	120.9(2)	C10–C11–C12	121.2(3)
N3–N4–C14	105.4(2)	C11–C12–C13	116.8(3)
C2–N5–C6	116.7(2)	C8–C13–C12	122.6(2)
N2–C1–N3	111.2(2)	N2–C13–C12	131.7(2)
H1–C1–N3	106(2)	N2–C13–C8	105.7(2)
H1–C1–N2	104(2)	N4–C14–C15	112.3(2)
N3–C1–C2	113.8(2)	C14–C15–C20	104.6(2)
N2–C1–C2	112.3(2)	C14–C15–C16	136.9(3)
H1–C1–C2	109(2)	C16–C15–C20	118.5(2)
N5–C2–C1	114.5(2)	C15–C16–C17	118.8(3)
C1–C2–C3	122.3(2)	C16–C17–C18	121.6(3)
N5–C2–C3	122.9(2)	C17–C18–C19	121.1(3)
C2–C3–C4	118.9(3)	C18–C19–C20	117.0(3)
C3–C4–C5	119.2(3)	C15–C20–C19	122.9(2)
C4–C5–C6	118.2(3)	N3–C20–C19	130.9(2)
N5–C6–C5	124.1(3)	N3–C20–C15	106.1(2)

TABLE 7. Selected angles (°) between the least-squares sets defined by the specified atoms for the free and coordinated ligand

1–N2, N1, C7, C8, C13	2–C1, H1, N2
3–N3, N4, C14, C15, C20	4–C1, H1, N3
5–C2, C3, C4, C5, C6, N5	6–C1, H1, C2
7–C8, C9, C10, C11, C12, C13	8–C15, C16, C17, C18, C19, C20

	1	2
Planes		
1–2	11.4(9)	3.9(3)
3–4	21.7(9)	4.3(9)
5–6	85.6(9)	5.8(7)
1–3	79.7(1)	58.4(4)
1–5	70.2(1)	59.1(3)
3–5	61.4(1)	63.9(4)
1–7	0.9(1)	0.8(3)
3–8	2.2(1)	2.8(4)

On the other hand, defining a plane through the three atoms (N2, N3 and C2) bonded to the central C1 atom, we have observed that the three pyridine-type nitrogen atoms of the ligand (N1, N4 and N5) adopt an $\alpha\beta\alpha$ conformation if we assign the α conformation to the region lying on the same side of the plane as the C1–H1 bond and β to the other.

The crystal of complex **2** consists of $[Rh(BIPM)(NBD)]^+$ mononuclear cations and hexafluorophos-

TABLE 8. Bond distances (Å) and selected angles (°) for **2**

Rh–N1	2.16(1)	C4–C5	1.35(2)
Rh–N4	2.249(7)	C5–C6	1.39(2)
Rh–N5	2.166(8)	C7–C8	1.41(2)
Rh–C21	2.09(2)	C8–C9	1.40(2)
Rh–C22	2.14(2)	C8–C13	1.40(1)
Rh–C23	2.65(2)	C9–C10	1.36(2)
Rh–C24	2.11(1)	C10–C11	1.40(2)
Rh–C25	2.21(1)	C11–C12	1.35(2)
Rh–C26	2.66(2)	C12–C13	1.41(1)
Rh–G1	2.00(2)	C14–C15	1.42(1)
Rh–G2	2.05(1)	C15–C16	1.41(1)
N1–N2	1.368(9)	C15–C20	1.389(9)
N1–C7	1.32(2)	C16–C17	1.35(2)
N2–C1	1.45(1)	C17–C18	1.40(1)
N2–C13	1.36(2)	C18–C19	1.36(1)
N3–N4	1.35(1)	C19–C20	1.39(2)
N3–C1	1.454(7)	C21–C22	1.38(2)
N3–C20	1.38(1)	C21–C26	1.46(2)
N4–C14	1.327(8)	C22–C23	1.38(3)
N5–C2	1.34(1)	C23–C24	1.50(3)
N5–C6	1.35(2)	C24–C25	1.34(2)
C1–C2	1.51(2)	C25–C26	1.35(4)
C2–C3	1.39(1)	C26–C27	1.62(4)
C3–C4	1.37(2)	C23–C27	1.60(2)
		H1–C1	1.013(8)
G1–Rh–G2	68.4(4)	N5–Rh–C24	160.5(4)
C25–Rh–G2	17.6(6)	N5–Rh–C22	100.9(4)
C25–Rh–G1	67.5(6)	N5–Rh–C21	98.5(5)
C24–Rh–G2	18.4(5)	N4–Rh–G2	106.3(4)
C24–Rh–G1	71.6(5)	N4–Rh–G1	140.0(6)
C24–Rh–C25	36.0(5)	N4–Rh–C25	95.7(4)
C22–Rh–G2	68.7(4)	N4–Rh–C24	116.3(4)
C22–Rh–G1	18.7(6)	N4–Rh–C22	158.7(6)
C22–Rh–C25	73.8(6)	N4–Rh–C21	120.8(5)
C22–Rh–C24	65.6(5)	N4–Rh–N5	81.6(3)
C21–Rh–G2	70.4(4)	N1–Rh–G2	105.5(4)
C21–Rh–G1	19.2(5)	N1–Rh–G1	136.5(4)
C21–Rh–C25	63.4(5)	N1–Rh–C25	118.9(5)
C21–Rh–C24	79.5(4)	N1–Rh–C24	90.7(5)
C21–Rh–C22	37.9(5)	N1–Rh–C22	117.8(4)
N5–Rh–G2	168.7(4)	N1–Rh–C21	155.7(3)
N5–Rh–G1	100.3(5)	N1–Rh–N5	83.4(3)
N5–Rh–C25	157.3(7)	N1–Rh–N4	83.5(3)
C25–C26–C21	107(1)		
C24–C23–C22	106(3)		
C25–C26–C27	95(2)		
C21–C26–C27	100(1)		
C22–C23–C27	99(1)		
C24–C23–C27	98(1)		

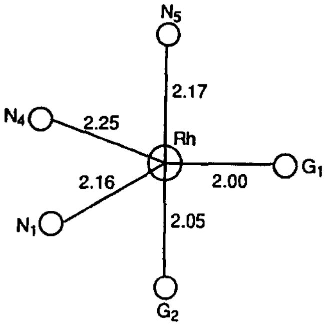


Fig. 3. Details of the coordination around Rh in complex 2.

phate anions. The rhodium atom is pentacoordinate, and the geometry corresponds to a distorted trigonal bipyramid as depicted in Fig. 2. Selected bond distances and bond angles are given in Table 8.

The N5 atom and the centroid (G2) of the C24–C25 olefinic bond are in the apical positions, the equatorial ones being occupied by N1, N4 and the centroid (G1) of the C21–C22 double bond (Fig. 3). The plane defined by G1, N1 and N4 contains the Rh atom and forms an angle of 92.0(3) with the G2–Rh–N5 axis. Some geometrical features are noteworthy:

(i) The distance between the rhodium atom and the pyridine N5 is longer than found in related five-coordinate compounds [4].

(ii) C22–C23 of 1.38(3) and C25–C26 of 1.35(4) Å are shorter than values which correspond to single bonds.

(iii) Rh–C26 and Rh–C23 of 2.65(2) and 2.66(2) Å are also shorter than usually observed in related Rh (NBD) complexes [25].

Finally, as indicated in Table 8, the coordination does not significantly affect the bond length and angles in the BIPM ligand, but, as expected [26], important changes in the dihedral angles are observed (Table 7).

4. Supplementary material available

Tables giving additional crystallographic details and anisotropic thermal parameters for compounds (1) (27 pages) and (2) (43 pages) can be obtained from the authors.

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