Inorganica Chimica Acta, *115* (1986) 65–73

Rhodium(I) and Iridium(I) Complexes of 2,2′-Dipyridylamine and its Deprotonated Form*

LUIS A. ORO**, MIGUEL A. CIRIANO, FERNANDO VIGURI

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

CONCEPCION FOCES-FOCES and FELIX H. CANO

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

Received October 15, 1985

Abstract

The syntheses and properties of cationic and neutral rhodium(I) and iridium(I) complexes with the 2,2′-dipyridylamine ligand (Hdipy) and its deprotonated form (dipy) are reported. Representative general formulae are: $[M(L_2)(Hdipy)]ClO_4$ (M = Rh, Ir; L_2 = diolefin, L = CO), $[M(CO)_2(Hdipy)][MCl_2(CO)_2]$, [MCl(diolefin)(Hdipy)] and [M(dipy)(diolefin)]. The latter complex still has an amide nitrogen available for coordination and is used for the syntheses of the binuclear complexes $[(diolefin)Rh(\mu\text{-}dipy)Rh(CO)(PPh_3)_2]ClO_4$ and $[Rh_2(\mu\text{-}dipy)Cl(diolefin)_2]$.

The crystal and molecular structure of the complex [Rh(dipy)(nbd)] (nbd = 2,5-norbornadiene) has been determined by single-crystal X-ray methods. Crystals are triclinic, space group $P\bar{1}$ with cell constants a = 12.3651(4), b = 12.4386(3), c = 10.0809(3) Å, α = 103.209(2), β = 110.278(2), and γ = 88.125(2)°, and Z = 4. The final R and R_w values were 0.033 and 0.039 for 4180 observations. The Rh atoms in the two independent molecules in the unit cell present similarly distorted square-planar geometries with both chelate ligands coordinated to each metal atom.

Introduction

A large number of diolefin or dicarbonyl–rhodium(I) complexes containing chelating nitrogen donor ligands are known [1, 2] and some of them are active catalyst precursors for hydrogen-transfer reactions [3, 4]. Rhodium(I) complexes derived from diimino analogues of β-diketones, dipyrromethenes and related macrocyclic ligands [1, 2] present a six-membered chelate ring possessing a delocalized electronic structure; interestingly, crystallographic studies on some dicarbonyl derivatives show the presence of short intermolecular Rh–Rh distances [5, 6].

As a continuation of our studies on rhodium(I) complexes with heterocyclic nitrogen-donor ligands [7, 8] we have now focused our attention on the ligand 2,2′-dipyridylamine (Hdipy), which has the appropriate features to behave as a bidentate chelating anionic or neutral ligand towards rhodium(I), affording neutral or cationic complexes with six-membered rings. The coordinative behaviour of this ligand has been reviewed by McWhinnie [9]. Recently, investigations into physical properties of the complexes $[M(Hdipy)_n(dipy)_{2-n}(Cl)_2]^{(n-1)+}$ (M = Rh(III), Ir(III)) and $[Ru(Hdipy)_n(dipy)_{3-n})]^{(n-1)+}$ have shown unique redox and spectroscopic properties [10–12]. On the other hand, the ligand 2,2′-dipyridylamine is able to stabilize the first well-characterized stable Cu(I) complexes with ethylene and carbon monoxide [13]. Consequently, an exploration of the chemistry of 2,2′-dipyridylamine complexes of rhodium(I) and iridium(I) might be of interest.

Experimental

The complexes $[RhCl(diolefin)]_2$ (diolefin = 1,5-cyclooctadiene (cod) [14], 2,5-norbornadiene (nbd) [15], tetrafluorobenzobarrelene (tfb) [16], $[IrCl(cod)]_2$ [17], $[IrCl(tfb)_2]$ [18] and $[Rh(CO)(PPh_3)_2(OCMe_2)]ClO_4$ [19] were prepared by published methods. Reactions were carried out at room temperature. Solvents were purified and dried by standard methods and deoxygenated prior to use. The catalytic transfer hydrogenation reactions were carried out as previously described [3].

---

*Dedicated to Prof. Rafael Uson on the occasion of his 60th birthday.

**Author to whom correspondence should be addressed.

0020-1693/86/$3.50

TABLE I. Analytical and Physical Data for Compounds **I–XXI**

	Compound	Colour	Yield (%)	Analysis^a			Molecular weight^a	Molar conductivity (ohm^{-1} cm^2 mol^{-1})
				C%	H%	N%		
I	{Rh(cod)(Hdipy)]ClO$_4$·Me$_2$O	yellow	90	46.3 (46.72)	5.1 (5.04)	7.85 (7.78)		109
II	[Rh(nbd)(Hdipy)]ClO$_4$	yellow	87	43.8 (43.84)	3.7 (3.68)	9.2 (9.02)		108
III	[Rh(tfb)(Hdipy)]ClO$_4$	yellow	81	44.4 (44.06)	2.85 (2.52)	7.0 (7.00)		120
IV	[Ir(cod)(Hdipy)]ClO$_4$	yellow	81	37.5 (37.86)	3.7 (3.88)	7.6 (7.36)		97
V	[Rh(CO)$_2$(Hdipy)]ClO$_4$	pale-yellow	85	33.5 (33.55)	2.1 (2.11)	10.1 (9.78)		130
VII	[Rh(dipy)(cod)]	yellow	89	56.5 (56.70)	5.3 (5.28)	11.1 (11.02)	406 (381)	
VIII	[Rh(dipy)(nbd)}	yellow	92	56.0 (55.90)	4.5 (4.41)	11.45 (11.50)	344 (365)	
IX	[Rh(dipy)(tfb)]	yellow	85	52.2 (52.92)	2.7 (2.83)	8.5 (8.41)	540 (499)	
X	[Ir(dipy)(cod)}	yellow	88	45.6 (45.94)	4.2 (4.28)	9.0 (8.93)	990 (470)	
XI	[Ir(dipy)(tfb)]	yellow	75	44.5 (44.89)	2.1 (2.40)	7.3 (7.14)	630 (588)	
XII	[RhCl(nbd)(Hdipy)]	yellow	94	49.8 (50.82)	4.3 (4.26)	10.3 (10.46)		
XIII	[RhCl(tfb)(Hdipy)]	yellow	79	49.1 (49.32)	2.9 (2.82)	7.9 (7.84)		
XIV	[IrCl(cod)(Hdipy)]	yellow	77	42.1 (42.63)	3.8 (4.17)	8.4 (8.28)	645 (507)	11
XV	[Rh(CO)$_2$(Hdipy)][RhCl$_2$(CO)$_2$]	orange	80	30.1 (30.02)	1.6 (1.62)	7.4 (7.50)		102
XVI	[Ir(CO)$_2$(Hdipy)][IrCl$_2$(CO)$_2$]	green	79	22.8 (22.76)	1.3 (1.30)	5.8 (5.69)		113
XVII	[(nbd)Rh(μ-dipy)Rh(CO)(PPh$_3$)$_2$]-ClO$_4$·CH$_2$Cl$_2$	yellow	66	54.0 (53.81)	3.8 (3.85)	3.3 (3.49)		123
XVIII	[(tfb)Rh(μ-dipy)Rh(CO)(PPh$_3$)$_2$]-ClO$_4$	yellow	81	56.3 (56.50)	3.5 (3.54)	3.5 (3.35)		118
XIX	[Rh$_2$(μ-dipy)Cl(cod)$_2$]	yellow	67	49.3 (49.70)	5.3 (5.14)	6.8 (6.69)	626 (628)	
XX	[Rh$_2$(μ-dipy)Cl(nbd)$_2$]	yellow	69	48.3 (48.31)	4.0 (4.05)	7.0 (7.04)	643 (597)	
XXI	[Rh$_2$(μ-dipy)Cl(tfb)$_2$]	yellow	73	47.0 (47.27)	2.6 (2.33)	4.8 (4.86)	828 (864)	

[a] Found (calc.)%.

Measurements

Elemental analyses (Table I) were carried out with a Perkin-Elmer 240 B microanalyzer. Infrared spectra (range 4000–200 cm^{-1}) were recorded on a Perkin-Elmer 783 spectrophotometer using nujol mulls between polyethylene sheets or dichloromethane solutions in NaCl windows. Conductivities were measured in *ca.* 5×10^{-4} mol l^{-1} acetone solutions using a Philips 9501/01 conductimeter. Molecular weights were determined in chloroform with a

Knauer osmometer. The ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded with a Varian XL-200 spectrometer operating at 200.057 and 80.948 MHz, respectively.

Syntheses

*Preparation of [Rh(diolefin)(Hdipy)]ClO$_4$ (**I–III**) and [Ir(cod)(Hdipy)]ClO$_4$ (**IV**)*

A solution of [M(diolefin)(OCMe$_2$)$_x$]$^+$ (M = Rh, diolefin = cod, nbd, tfb; M = Ir, diolefin = cod), prepared by reaction of the appropriate compound [MCl(diolefin)]$_2$ (0.1 mmol) with AgClO$_4$ (42 mg, 0.2 mmol) in acetone (15 ml) for 15 min and further filtration, was added to a solution of 2,2'-dipyridylamine (34 mg, 0.2 mmol) in acetone. Evaporation of the resulting solutions under reduced pressure to *ca.* 1 ml and then addition of diethyl ether rendered complexes **I–IV** as crystals which were separated by filtration and vacuum-dried.

*Preparation of [M(CO)$_2$(Hdipy)]ClO$_4$ (M = Rh (**V**), Ir (**VI**)*

Dry carbon monoxide was bubbled through dichloromethane solutions (10 ml) of the complexes **II** and **IV** (0.15 mmol) for 15 min. Evaporation of these solutions to *ca.* 2 ml and addition of diethyl ether gave complexes **V** and **VI** as solids, which were filtered and vacuum-dried.

*Preparation of [M(dipy)(diolefin)] (M = Rh, diolefin = cod (**VII**), nbd (**VIII**), tfb (**IX**); M = Ir, diolefin = cod (**X**), tfb (**XI**)*

A solution of 2,2'-dipyridylamine (34 mg, 0.2 mmol) in dry diethylether (10 ml) was reacted with a solution of butyllithium (1.4 mol l^{-1} in hexane, 0.1 ml, 0.2 mmol) for 30 min to give a white suspension. The appropriate compound [MCl(diolefin)]$_2$ (0.1 mmol) was then added and the mixture was stirred for 30 min to give yellow or orange suspensions. The solvent was evaporated under vacuum and the residue was washed with a 1:1 mixture of acetone:water (5 ml) to yield yellow solids which were filtered and vacuum-dried. Complex **XI** was prepared from [IrCl(tfb)$_2$] (68 mg, 0.1 mmol) and the reaction time was 12 h.

Deprotonation and Protonation Reactions

(a) Reaction of the complexes of the type [Rh-diolefin)(Hdipy)]ClO$_4$ with potassium hydroxide

A suspension of the complex **I** or **II** (0.1 mmol) in methanol (10 ml) was reacted with a solution of potassium hydroxide (0.090 mol l^{-1}, 1.1 ml, 0.1 mmol) in methanol for 30 min to give yellow solutions. The solvent was evaporated to dryness under reduced pressure and the residue was extracted with dichloromethane. Complexes **VII** and **VIII** were isolated as solids by addition of hexane to concentrated solutions of the extracts.

(b) Reaction of [Rh(dipy)(nbd)] with HBF$_4$

Tetrafluoroboric acid (50% in water, 12.5 μl, 0.1 mmol) was added to a suspension of complex **VIII** (0.1 mmol) in acetone (10 ml) to give a yellow solution. Evaporation to *ca.* 1 ml and addition of diethyl ether gave yellow crystals of the complex [Rh(nbd)(Hdipy)]BF$_4$. Yield, 50%. *Anal.* Calc. for $C_{17}H_{17}N_3BF_4Rh$: C, 45.07; H, 3.78; N, 9.27. Found: C, 44.5; H, 3.9; N, 9.3%.

*(c) Reactions of the compolexes **VIII** and **IX** with hydrochloric acid*

To a suspension of the complexes **VIII** in acetone or **IX** (0.1 mmol) in diethyl ether (10 ml), hydrochloric acid (12 mol l^{-1} in water, 8.4 μl, 0.1 mmol) was added to give yellow solutions from which yellow solids precipited out. The solvent was evaporated under reduced pressure to *ca.* 2 ml and the solids **XII** and **XIII** (see below) were separated by filtration.

*Preparation of [MCl(diolefin)(Hdipy)] (M = Rh, diolefin = ndb (**XII**), tfb (**XIII**); M = Ir, diolefin = cod (**XIV**)*

2,2'-Dipyridylamine (34.4 mg, 0.2 mmol) was stirred with suspensions of the complexes [MCl(diolefin)]$_2$ (0.1 mmol) in dichloromethane (for **XII**), diethyl ether (for **XIII**) or acetone (for **XIV**) for 30 min to give yellow suspensions. The solvent was evaporated to *ca.* 2 ml and the solids were separated by filtration.

*Preparation of [M(CO)$_2$(Hdipy)][MCl$_2$(CO)$_2$] (M = Rh (**XV**), Ir (**XVI**)*

Through a suspension of the complex [MCl(cod)]$_2$ (M = Rh, Ir) (0.1 mmol) and 2,2'-dipyridylamine (17 mg, 0.1 mmol) in dichloromethane, carbon monoxide was bubbled for 15 min to give an orange solution of complex **XV** or a dark-green solid **XVI**. Addition of diethyl ether to the solution or suspension, respectively, produces complete crystallization of the complexes, which were separated by filtration.

*Preparation of the complexes [(diolefin)Rh(μ-dipy)Rh(CO)(PPh$_3$)$_2$]ClO$_4$ (diolefin = nbd (**XVII**), tfb (**XVIII**))*

Solid [Rh(CO)(PPh$_3$)$_2$(OCMe$_2$)]ClO$_4$ (41 mg, 0.05 mmol) was added to a dichloromethane solution (10 ml) of the complex [Rh(dipy)(diolefin)] (diolefin = nbd or tfb) (0.05 mmol). Evaporation of the resulting yellow solution to *ca.* 2 ml and addition of diethyl ether afforded crystals of the complex **XVII** or **XVIII**, respectively, which were separated by filtration.

TABLE II. Crystal Analysis Parameters at Room Temperature

Crystal data	
Formula	[Rh(dipy)(nbd)]
Crystal habit	yellow plate
Crystal dimensions (mm)	0.48 × 0.24 × 0.08
Symmetry	triclinic, $P\bar{1}$
Unit cell determination: least-squares fit to	91 reflexions, θ(Cu) < 45
Unit cell parameters	
a (Å)	12.3651(4)
b (Å)	12.4386(3)
c (Å)	10.0809(3)
α (°)	103.209(2)
β (°)	110.278(2)
γ (°)	88.125(2)
Packing	
V (Å^3)	1414.1(1)
Z	4
D (g cm^{-3})	1.716
M	365.239
F(000)	736
Experimental data	
Radiation and technique	Cu Kα, PW1100 diffractometer bisecting geometry
Monochromator	graphite oriented
Collection mode	$\omega/2\theta$, θ < 65, 1 × 1 det. apertures 1 min/ref., 1.5 scan width
Total independent data	4805
Observed data	4180, $I > 4\sigma(I)$
Stability	two reflexions every 90 min, no variation
μ (cm^{-1}), max. min. transmission factors	99.313, 0.489–0.116
Solution and refinement	
Solution	XRAY76 [20], Vax11/750
Refinement	least-squares on Fs, observed reflexions two blocks
Final shift/error	0.14
Number of variables	507
Degrees of freedom	3673
Ratio of freedom	8.2
Weighting scheme	empirical as to give no trends in $\langle w\Delta^2\rangle$ *vs.* $\langle F_o\rangle$ or $\langle \sin\theta/\lambda\rangle$
Maximum thermal values (Å^2)	U_{22} (C34) = 0.160(8)
Final F peaks	1.22 e Å^{-3} near the Rh atoms
Final R, R_w	0.033, 0.039
Atomic factors	International Tables for X-ray Crystallography [21]

TABLE III. Final Atomic Coordinates

Atom	x/a	y/b	z/c
Rh1	0.82113(2)	−0.01317(2)	0.08746(3)
N1	0.9621(3)	−0.1028(3)	0.0725(4)
C2	1.0583(4)	−0.0920(5)	0.1940(6)
C3	1.1528(5)	−0.1538(6)	0.2023(8)
C4	1.1499(6)	−0.2340(6)	0.0795(9)
C5	1.0562(6)	−0.2462(5)	−0.0427(8)
C6	0.9610(4)	−0.1778(4)	−0.0499(6)
N7	0.8777(4)	−0.1950(3)	−0.1814(5)
C8	0.7770(4)	−0.1463(4)	−0.2225(5)
C9	0.7100(6)	−0.1790(5)	−0.3739(7)
C10	0.6057(6)	−0.1385(6)	−0.4308(6)
C11	0.5640(5)	−0.0629(6)	−0.3379(7)
C12	0.6282(5)	−0.0326(5)	−0.1954(6)
N13	0.7335(3)	−0.0718(3)	−0.1336(4)
C21	0.8613(4)	0.0081(4)	0.3156(5)
C22	0.9032(4)	0.1017(4)	0.2892(5)
C23	0.8060(5)	0.1824(4)	0.2748(6)
C24	0.7183(4)	0.1231(4)	0.1287(6)
C25	0.6766(4)	0.0294(4)	0.1554(5)
C26	0.7392(4)	0.0327(4)	0.3149(6)
C27	0.7523(5)	0.1585(5)	0.3819(7)
Rh2	0.26220(2)	0.48534(2)	−0.09478(3)
N31	0.3987(3)	0.5943(3)	−0.0547(4)
C32	0.4295(4)	0.6047(4)	−0.1691(5)
C33	0.5116(5)	0.6771(4)	−0.1628(6)
C34	0.5690(4)	0.7479(4)	−0.0290(6)
C35	0.5416(4)	0.7404(4)	0.0883(5)
C36	0.4574(4)	0.6609(3)	0.0779(4)
N37	0.4448(3)	0.6588(3)	0.2042(4)
C38	0.3744(4)	0.5911(4)	0.2272(5)
C39	0.3902(7)	0.6023(7)	0.3753(6)
C40	0.3230(8)	0.5398(9)	0.4159(7)
C41	0.2392(6)	0.4642(6)	0.3110(6)
C42	0.2269(4)	0.4561(4)	0.1716(6)
N43	0.2919(3)	0.5174(3)	0.1266(4)
C55	0.0859(4)	0.4260(5)	−0.1752(6)
C54	0.1559(4)	0.3359(4)	−0.1661(6)
C53	0.1710(5)	0.2980(4)	−0.3134(6)
C52	0.2471(4)	0.3940(4)	−0.3066(5)
C51	0.1768(4)	0.4850(4)	−0.3164(5)
C56	0.0591(5)	0.4428(5)	−0.3289(6)
C57	0.0528(5)	0.3238(6)	−0.4163(7)

*Preparation of the complexes [Rh_2(μ-dipy)Cl(diolefin)$_2$] (diolefin = cod (**XIX**), nbd (**XX**), tfb (**XXI**))*

The complex [Rh(dipy)(diolefin)] (0.1 mmol) was mixed with a solution of the corresponding [RhCl(diolefin)]$_2$ (0.05 mmol) in dichloromethane (10 ml) to give a yellow solution. Concentration to *ca.* 1 ml under reduced pressure and addition of hexane gave the complexes **XIX**, **XX** and **XXI** as solids which were filtered and vacuum-dried.

X-ray Analysis

Crystal analysis parameters are given in Table II. The single crystal used was grown by slow diffusion of diethyl ether into a dichloromethane solution of the complex. The final atomic coordinates for the non-hydrogen atoms are given in Table III.

Results and Discussion

Addition of solutions of the cationic species $[M(diolefin)(Me_2CO)_x]^+$ (M = Rh, Ir) in acetone to 2,2'-dipyridylamine (Hdipy) in the same solvent gives the complexes of the type $[M(diolefin)(Hdipy)]ClO_4$ (M = Rh; diolefin = cycloocta-1,5-diene (cod) (**I**), norborna-2,5-diene (nbd) (**II**), tetrafluorobenzobarrelene (tfb) (**III**); M = Ir, diolefin = cod (**IV**)). After working-up, the complexes **I**–**IV** are isolated as air-stable microcrystalline solids in good yield (see Table I). Complex **I** crystallizes with one molecule of acetone and gives a strong band at 1713 cm^{-1}; it is also detected by elemental analyses. The infrared spectra of complexes **I**–**IV** show several bands associated to ν(N–H) in the 3350–3100 cm^{-1} region. The bands are also observed in the spectrum of the free ligand, along with the expected absorptions of the corresponding diolefin and anionic perchlorate (T_d). Complexes **I**–**IV** are 1:1 electrolytes in acetone in accord with the proposed formulae. The 200 MHz ^1H NMR spectrum of complex **II** in d_6-acetone consists of three multiplet resonances for both of the magnetically equivalent pyridyl rings between δ 8.1 and 7.0, and three resonances for the olefinic, tertiary and bridgehead protons of the nbd ligand. Integration gives the ratio 8(dipy): 4:2:2. The ^1H NMR spectrum is consistent with a C_{2v} symmetry of the complex, as observed for the compound *trans*-$[RuCl_2(bipy)(nbd)]$ [22], and suggests a square-planar structure of the complex where the Hdipy acts as a bidentate and chelating ligand.

Bubbling carbon monoxide through dichloromethane solutions of complexes **I** or **IV** gives yellow solutions of $[Rh(CO)_2(Hdipy)]ClO_4$ (**V**) and $[Ir(CO)_2(Hdipy)]ClO_4$ (**VI**) which show two strong ν(CO) bands at 2095, 2035 and 2085, 2020 cm^{-1}, respectively; these bands are characteristic of a *cis*-dicarbonyl metal structure. Complex **V** is isolated as a yellow analytically pure solid, whereas $[Ir(CO)_2(Hdipy)]ClO_4$ is a navy-blue solid that does not give satisfactory microanalysis. Concentrated dichloromethane solutions of the latter complex have a blue–green colour and show weak shoulders (at 2075 and 1985 cm^{-1}) on the two strong bands. In the solid state (Nujol), the complex displays four ν(CO) bands at 2100vs, 2075s, 2020vs and 1990m cm^{-1}. The deep-blue colour and the splitting of the ν(CO) bands of the iridium complex are indicative of the existence of intermolecular metal–metal interactions in the solid state which are not present in the related rhodium complex **V*** because of the concentration of the metal d_{z^2} orbitals [23]. Complexes **V** and **VI** are 1:1 electrolytes in acetone in accord with the proposed formulae.

The amine proton becomes more acidic on complexation and thus the complex $[Rh(nbd)(Hdipy)]ClO_4$ reacts with potassium hydroxide in methanol to give crude [Rh(dipy)(nbd)]. The general route to the complexes [M(dipy)(diolefin)] [M = Rh, diolefin = cod (**VII**), nbd (**VIII**), tfb (**IX**); M = Ir, diolefin = cod (**X**), tfb (**XI**)) consists of reacting the compounds $[MCl(diolefin)]_2$ or $[Ir Cl(tfb)_2]$ with a suspension of lithium 2,2'-dipyridylamide [24] in diethyl ether. Complexes **VII**–**XI** are air-stable solids which show in their IR spectra the bands of the corresponding diolefin and 2,2'-dipyridylamine, except those associated with ν(NH) in the 3350–3100 cm^{-1} region. Their molecular weights in chloroform solution are those expected for mononuclear complexes, except for complex **X** which apparently is binuclear.

The ^1H NMR spectrum of complex [Rh(dipy)(nbd)], for instance, displays four well-resolved signals in the aromatic region arising from the four protons of both of the magnetically equivalent pyridyl rings and three multiplet signals from the olefinic, tertiary and bridgehead protons of the diolefin; this pattern is in accordance with that of a molecule of C_{2v} symmetry as found by X-ray diffraction methods. Square-planar structures of C_{2v} symmetry are proposed for the other diolefin neutral complexes **IX**–**XI** on the bases of their ^1H NMR spectra (see Table IV).

The neutral complex [Rh(dipy)(nbd)] reacts with noncoordinating protonic acids such as tetrafluoroboric acid to regenerate the cationic complex $[Rh(nbd)(Hdipy)]BF_4$. Coordinating acids, such as hydrochloric acid, react with the neutral complexes **VIII** and **IX** to give yellow materials analysing as $[RhCl(nbd)(Hdipy)]_x$ and $[RhCl(tfb)(Hdipy)]_x$, respectively. These compounds and $[IrCl(cod)(Hdipy)]_x$ (**XIV**) can be prepared by reaction of the complexes $[RhCl(diolefin)]_2$ or $[IrCl(cod)]_2$ with the ligand in a 1:2 molar ratio in dichloromethane or acetone. The low solubility of the rhodium complexes in organic solvents precludes further characterization. Nevertheless, they react with thallium(I) acetylacetonate or potassium hydroxide to re-form complexes **VIII** or **IX**. The iridium complex is soluble in dichloromethane and chloroform and slightly soluble in acetone. Solutions of this complex in acetone show a low but noticeable conductivity (11 ohm^{-1} cm^2 mol^{-1} for 6.1 × 10^{-4} mol l^{-1} solution**). On the other hand, molecular weight measurements suggest $x = 3$.

The ^1H NMR spectrum of this complex in $CDCl_3$ shows intense resonances for a symmetrical species which is the most abundant in solution (given

---

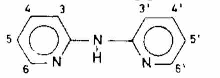
*Similar features are shown by the complexes $[M(CO)_2]_2(C_2O_4)$ (M = Rh, Ir) [23b].

**Calculated for molecular weight = 507.

TABLE IV. ^1H NMR Data for Selected Complexes[a]

Compound	Solvent	Heterocyclic ring protons				Diolefin
		$H^{3/3'}$	$H^{4/4'}$	$H^{5/5'}$	$H^{6/6'}$	
I	d_6-acetone	7.40dt[b]	8.00ddd	7.11ddd	7.37dt[b]	4.34(q[b],4H,olefinic),3.95(m,2H,CH),1.54(t,1.70Hz,2H,CH_2)
VIII	$CDCl_3$	7.07d	7.32ddd	6.31ddd	6.75d	3.89(t[b],4H,olefinic),3.83(m,2H,CH),1.55(t,1.40Hz,2H,CH_2)
IX	$CDCl_3$	7.26d	7.41ddd	6.35ddd	6.70d	5.54(m,2H,CH),3.73(m,4H,olefinic)
X	$CDCl_3$	7.11d	7.37ddd	6.37ddd	7.70d	3.85(m,4H,olefinic),2.30(m,4H,CH_2),1.73m,4H,CH_2)
XI	$CDCl_3$	6.86d	7.50m	6.38t[b]	7.50m	5.48(m,2H,CH),2.96(m,4H,olefinic)
XIV	$CDCl_3$	8.18m	7.69ddd	6.92ddd	8.09d	3.84(m,4H,olefinic),2.3(m,4H,CH_2),1.6(m,4H,CH_2)
XV	d_6-acetone	7.68d	8.17ddd	7.36ddd	8.80d	

[a]Chemical shifts in ppm from TMS at 20 °C. [b]Apparent; dt = doublet of triplets; ddd = double doublet of doublets; m = multiplet; heterocyclic proton labelling:



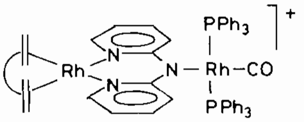


Fig. 1. Proposed structure for the species $[(\text{diolefin})Rh(\mu\text{-dipy})Rh(CO)(PPh_3)_2]^+$.

in Table IV) and weak resonances in the aromatic and olefinic regions due to the presence of other species, which accounts for the anomalous molecular weight and conductivity.

Bubbling carbon monoxide through solutions of complexes **VIII** or **X** gives insoluble black or navy-blue materials, respectively, which show strong and broad terminal $\nu(CO)$ bands; they were not further investigated. On the other hand, if carbon monoxide is bubbled through a suspension of $[RhCl(cod)]_2$ or $[IrCl(cod)]_2$ and the ligand in dichloromethane in molar ratio 1:1, solutions of the complexes of the type $[M(CO)_2(Hdipy)][MCl_2(CO)_2]$ (M = Rh (**XV**), Ir (**XVI**)) are found.

The rhodium complex **XV** is an orange solid whereas the iridium complex **XVI** is a dark-green dicroic solid showing close metal–metal intermolecular contacts in the solid state. Both complexes show two intense $\nu(CO)$ bands of the anion $[MCl_2(CO)_2]^-$ and those reported above for the cation at 2090, 2060, 2020, 1985 cm^{-1} (complex **XV**) and 2080, 2045, 2000, 1965 (complex **XVI**) in the solid state. The ^1H NMR spectrum of complex **XV** shows four well-resolved resonances for the four sets of two magnetically equivalent protons of both pyridyl rings, in accordance with a square planar structure in which the ligand is bidentate and chelating.

The complexes of the type [Rh(dipy)(diolefin)] still have an amide nitrogen available for coordination and they act as ligands on reactions with species that easily provide a vacant site. Thus, binuclear cationic complexes of the type $[(\text{diolefin})Rh(\mu\text{-dipy})Rh(CO)(PPh_3)_2]ClO_4$ (diolefin = nbd (**XVII**), tfb (**XVIII**)) are obtained by reaction of complexes **VIII** and **IX** with $[Rh(CO)(PPh_3)_2(OCMe_2)]ClO_4$ [19] in dichloromethane. Complex **XVII** crystallized with dichloromethane and both **XVII** and **XVIII** are air-stable solids which behave as 1:1 electrolytes in acetone solution. They show a single strong terminal $\nu(CO)$ band at 1990 and 1995 cm^{-1}, respectively, in dichloromethane.

The $^{31}P\{^1H\}$ NMR spectrum of **XVII** displays a resonance doublet at 34.7 ppm ($^1J_{RhP}$: 123 Hz) for both of the magnetically equivalent phosphorus nuclei which should be attached to the same rhodium atom and *trans* to each other. The coupling constant is in the range reported for other *trans*-bis(triphenylphosphine)rhodium complexes (124–137 Hz) [25]. The spectroscopic data fit well with the structure of Fig. 1.

Interestingly, the complexes [Rh(dipy)(diolefin)] produce bridge-cleavage reactions of the complexes $[RhCl(\text{diolefin})]_2$ to give binuclear neutral complexes of the type $[(\text{diolefin})Rh(\mu\text{-dipy})RhCl(\text{diolefin})]$ (**XIX**–**XXI**). They are air-stable solids and their molecular weights in solution are in accordance with the proposed formulae. Their ^1H NMR spectra show broad signals for the protons of the dipy and diolefin ligands; these signals do not allow us to confirm their structures, although a structure similar to that of complex **XVII** is expected.

Finally, the [M(dipy)(diolefin)] and $[M(\text{diolefin})Hdipy)]ClO_4$ complexes (M = Rh, diolefin = cod, nbd; M = Ir, diolefin = cod) are active catalyst precursors, in the presence of potassium hydroxide, for the transfer of hydrogen in refluxing isopropanol to acetophenone or cyclohexene [3]. The results show that acetophenone is reduced more rapidly than cyclohexene, as expected for bidentate nitrogen-donor ligands [3a]. Typical conversions (%) after two hours are in the range 40–80% for acetophenone and below 20% for cyclohexene.

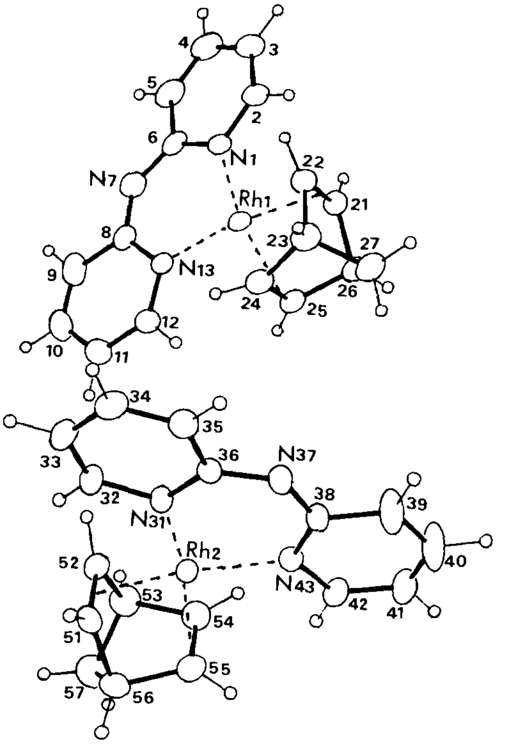


Fig. 2. View of the asymmetric unit showing the atomic numbering of [Rh(dipy)(nbd)]. Carbon symbols are omitted for clarity.

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

Rh1–N1	2.069(4)	Rh2–N31	2.068(4)
Rh1–N13	2.076(3)	Rh2–N43	2.076(4)
Rh1–C212	2.013(3)	Rh2–C512	1.999(3)
Rh1–C245	2.018(4)	Rh2–C545	2.023(4)
N1–C2	1.364(6)	N31–C32	1.365(7)
N1–C6	1.363(6)	N31–C36	1.364(5)
C2–C3	1.366(8)	C32–C33	1.355(8)
C3–C4	1.391(11)	C33–C34	1.391(6)
C4–C5	1.350(9)	C34–C35	1.361(9)
C5–C6	1.420(8)	C35–C36	1.420(7)
C6–N7	1.342(6)	C36–N37	1.341(7)
N7–C8	1.340(7)	N37–C38	1.341(7)
C8–C9	1.430(7)	C38–C39	1.411(8)
C9–C10	1.350(10)	C39–C40	1.373(15)
C10–C11	1.389(10)	C40–C41	1.388(10)
C11–C12	1.348(7)	C41–C42	1.341(9)
C12–N13	1.362(6)	C42–N43	1.373(8)
N13–C8	1.369(7)	N43–C38	1.352(5)
C212–Rh1–C245[a]	71.2(2)	C512–Rh2–C545[a]	71.0(1)
N13–Rh1–C245	99.6(2)	N43–Rh2–C545	99.9(2)
N1–Rh1–C212	98.6(2)	N31–Rh2–C512	99.3(1)
Ni–Rh1–N13	90.6(2)	N31–Rh2–N43	89.8(1)
Rh1–N1–C6	123.3(3)	Rh2–N31–C36	124.3(4)
Rh1–N1–C2	118.4(3)	Rh2–N31–C32	118.3(3)
C2–N1–C6	118.1(4)	C32–N31–C36	117.3(4)
N1–C2–C3	124.2(5)	N31–C32–C33	125.6(5)
C2–C3–C4	117.9(6)	C32–C33–C34	117.5(5)
C3–C4–C5	119.3(7)	C33–C34–C35	119.0(5)
C4–C5–C6	121.6(6)	C34–C35–C36	121.7(5)
C5–C6–N7	114.6(5)	C35–C36–N37	114.9(4)
N1–C6–N7	126.6(5)	N31–C36–N37	126.3(4)
N1–C6–C5	118.8(5)	N31–C36–C35	118.9(4)
C6–N7–C8	129.1(5)	C36–N37–C38	127.8(4)
N7–C8–N13	126.3(5)	N37–C38–N43	127.7(4)
N7–C8–C9	115.1(5)	N37–C38–C39	113.9(5)
C9–C8–N13	118.6(5)	C39–C38–N43	118.4(5)
C8–C9–C10	121.8(6)	C38–C39–C40	120.6(7)
C9–C10–C11	118.2(6)	C39–C40–C41	120.0(6)
C10–C11–C12	119.3(6)	C40–C41–C42	117.5(7)
C11–C12–N13	124.3(5)	C41–C42–N43	124.2(5)
C8–N13–C12	117.7(4)	C38–N43–C42	119.2(4)
Rh1–N13–C12	118.8(3)	Rh2–N43–C42	117.2(3)
Rh1–N13–C8	123.5(3)	Rh2–N43–C38	123.5(3)

[a] C212, C245, C512 and C545 are the midpoints of the olefinic bonds.

Structure of [Rh(dipy)(nbd)]

The crystal structure consists of an asymmetric unit of two independent molecules of the complex which do not display structurally significant differences. Figure 2 is a view of the asymmetric unit showing the atomic numbering. Table V lists distances and angles for both molecules. In the structure, each Rh atom is in a roughly square-planar environment coordinated to chelating dipy, through both pyridinic nitrogen atoms and nbd ligands. The Rh–N distances and Rh-midpoints of the olefinic bonds are slightly different; the larger Rh-midpoint is opposite to the shorter Rh–N distance. Furthermore, the angle centered at the Rh atom in the Rh(nbd) moiety is remarkably narrower than 90°. The plane defined by the RhN_2 entity and that defined by the Rh atom and the midpoint of the olefinic bonds form angles of 2.8(1) and 2.7(1)° (Table V).

The dipy ligand shows a pattern of bond lengths and angles in the complex different from that of the parent compound, Hdipy [26]. The two bridging C–N bond distances are alike (mean value 1.341 Å); they are similar to those found in the related neutral complex $[Cu(dipy)_2]$ [27] and significantly shorter (4.8 σ_p) than in the free Hdipy ligand and in the complexes $\{[CuI(Hdipy)_2]_2\}I(ClO_4)$ [28] and $[Cu(C_2H_4)(Hdipy)]ClO_4$ [13]. Although there are no bond interactions at all between the metal atom and the bridgehead nitrogen, the angles centered at this atom show similar values as in Hdipy, where there is a hydrogen bond. Moreover, the angles involving the carbon atom of the pyridine ring attached to the bridging nitrogen decrease in the order: N(bridge)–C–N > C–C–N > C–C–N(bridge). The ring angles at C(12) and at C(5) and their analogues in the rings of the two dipy ligands are significantly higher than the other endocyclic ones.

TABLE VI. Selected Torsion Angles (°) and Least-square Planes

Rh1–N1–C6–N7	9.1(7)	Rh2–N31–C36–N37	7.2(6)
N1–C6–N7–C8	–1.8(9)	N31–C36–N37–C38	1.1(8)
C6–N7–C8–N13	–4.9(9)	C36–N37–C38–N43	–7.5(8)
N7–C8–N13–Rh1	2.8(7)	N37–C38–N43–Rh2	4.1(7)
C8–N13–Rh1–N1	2.7(4)	C38–N43–Rh2–N31	2.3(4)
N13–Rh1–N1–C6	–8.0(4)	N43–Rh2–N31–C36	–7.4(4)
N1,C2,C3,C4,C5,C6	($\chi^2 = 48.9$)		
C8,C9,C10,C11,C12,N13	($\chi^2 = 0.24$)	7.5(2)	
N31,C32,C33,C34,C35,C36	($\chi^2 = 42.1$)		
C38,C39,C40,C41,C42,N43	($\chi^2 = 0.44$)	8.4(2)	
N1,Rh1,N13			
C212,Rh1,C245		2.8(1)	
N31,Rh2,N43			
C512,Rh2,C545		2.7(1)	

Least-squares planes calculations (Table VI) indicate that the dipy ligand as a whole is not planar. As it appears for Hdipy, a pyridine ring shows greater atom deviations to their plane than the other (χ^2 values of 48.9, 42.1 *vs.* 0.24, 0.44 and *vs.* the expected one of 7.81, see Table VI). The chelate rings Rh(1), N(1), C(6), N(7), C(8), N(13) and Rh(2), N(31), C(36), N(37), C(38), N(43) adopt diplanar conformations [29] at the C(6)–N(7)/C(8)–N(13) and C(36)–N(37)/C(38)–N(43) bonds, distorted towards a boat conformation at the C(6)–N(7)/Rh(1)–N(13) and C(36)–N(37)/Rh(2)–N(43) bonds (see Table VI) (Cremer and Pople parameters [30]: q_2 = 0.086(4), 0.091(4) Å, q_3 = 0.036(4), 0.024(4) Å, ϕ_2 = 42(3), 36(3)° and θ = 67(3), 75(2)°, respectively, compared with those of perfect diplanar boat conformations θ_2 = 30, 60° and ϕ = 67.5, 90°).

The nbd ligands show the usual geometrical features found in other complexes of this ligand [31].

Acknowledgements

We thank the Comisión Asesora de Investigación Científica y Técnica (C.A.I.C.Y.T.) for financial support (Project 1790/82), and Prof. S. García-Blanco for facilities.

References

1 R. P. Hughes, in G. Wilkinson, F. G. A. Stone and E. W. Abel (eds.), 'Comprehensive Organometallic Chemistry', Vol. 5, Pergamon, Oxford/New York, 1982, p. 288.

2 R. S. Dickson, 'Organometallic Chemistry of Rhodium and Iridium', Academic Press, New York/London, 1982, p. 117.

3 (a) R. Usón, L. A. Oro, R. Sariego and M. A. Esteruelas, *J. Organomet. Chem., 214,* 399 (1981). (b) L. A. Oro, M. P. Lamata and M. Valderrama, *Transition Met. Chem., 8,* 48 (1983) and refs. therein.

4 (a) R. Spogliarich, G. Zassinovich, G. Mestroni and M. Graziani, *J. Organomet. Chem., 179,* C45 (1979); (b) G. Zassinovich, G. Mestroni and A. Camus, *J. Organomet. Chem., 168,* C37 (1979) and refs. therein.

5 P. W. DeHaven and V. L. Goedken, *Inorg. Chem., 18,* 827 (1979) and refs. therein.

6 A. Takenaka, Y. Sasada, H. Ogoshi, T. Omura and Z. I. Yoshida, *Acta Crystallogr., Sect. B, 31,* 1 (1975).

7 A. Tiripicchio, M. Tiripicchio-Camellini, R. Usón, L. A. Oro, M. A. Ciriano and F. Viguri, *J. Chem. Soc., Dalton Trans.,* 125 (1984).

8 L. A. Oro, M. A. Ciriano, B. E. Villarroya, A. Tiripicchio and F. J. Lahoz, *J. Chem. Soc., Chem. Commun.,* 521 (1984); *J. Chem. Soc., Dalton Trans.,* 1891 (1985) and refs. therein.

9 W. R. McWhinnie, *Coord. Chem. Rev., 5,* 293 (1970).

10 W. L. Huang, D. P. Segers and M. K. DeArmond, *J. Phys. Chem., 85,* 2080 (1981).

11 D. P. Segers and M. K. DeArmond, *J. Phys. Chem., 86,* 3768 (1982).

12 D. E. Morris, Y. Ohsawa, D. P. Segers, K. M. DeArmond and K. W. Hanck, *Inorg. Chem., 23,* 3010 (1984).

13 J. S. Thompson and J. F. Whitney, *Inorg. Chem., 23,* 2813 (1984).

14 G. Giordano and R. H. Crabtee, *Inorg. Synth., 19,* 218 (1979).

15 E. W. Abel, M. A. Bennett and G. Wilkinson, *J. Chem. Soc.,* 3178 (1959).

16 D. M. Roe and G. Massey, *J. Organomet. Chem., 28,* 273 (1971).

17 J. L. Herde, J. C. Lambert and C. V. Senoff, *Inorg. Synth., 15,* 18 (1974).

18 R. Usón, L. A. Oro, D. Carmona, M. A. Esteruelas, C. Foces-Foces, F. H. Cano and A. Vazquez de Miguel, *J. Organomet. Chem., 273,* 111 (1984).

19 A. J. Deeming and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.,* 1259 (1980).

20 J. M. Stewart (ed.), P. A. Machin, C. W. Dickinson, H. L. Ammon, N. Heck and N. Flack (co-eds.), 'The X-ray System of Crystallographic Programs', Technical Report TR446, Computer Science Center, University of Maryland, 1976.

21 'International Tables for X-Ray Crystallography', Vol. 4, Kynoch Press, Birmingham, 1974.

22 B. P. Sullivan, J. A. Baumann, T. J. Meyer, D. J. Salmon, H. Lehmann and A. Ludi, *J. Am. Chem. Soc., 99,* 7368 (1977).

23 (a) P. B. Hitchcock, S. Morton and J. F. Nixon, *J. Chem. Soc., Dalton Trans.*, 1295 (1985); (b) S. Morton and J. F. Nixon, *J. Organomet. Chem., 282*, 123 (1985).
24 D. Barr, W. Clegg, R. E. Mulvey and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 469 (1984) and refs. therein.
25 P. S. Pregosin and R. W. Kunz, '^{31}P and ^{13}C NMR of Transition Metal Complexes', Springer-Verlag, Heidelberg, 1979, p. 111.
26 J. E. Johnson and R. A. Jacobson, *Acta Crystallogr., Sect. B, 29*, 1669 (1973).
27 O. R. Rudig, T. Brueckner, B. K. Hulburt, R. K. Schlatzer, T. L. Venable and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 196 (1981).
28 J. E. Johnson and R. A. Jacobson, *J. Chem. Soc., Dalton Trans.*, 580 (1973).
29 R. Bucourt and D. Hainant, *Bull. Soc. Chim. Fr., 2*, 1366 (1965).
30 D. Cremer and J. Pople, *J. Am. Chem. Soc., 97*, 1354 (1975).
31 R. Usón, L. A. Oro, M. A. Ciriano, M. M. Naval M. C. Apreda, C. Foces-Foces, F. H. Cano and S. García-Blanco, *J. Organomet. Chem., 256*, 331 (1983).