

## 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,  $L = CO$ ),  $[M(CO)_2(Hdipy)] \cdot [MCl_2(CO)_2]$ ,  $[MCl(diolefin)(Hdipy)]$  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  $[(diolefin)Rh(\mu-dipy)Rh(CO)(PPh_3)_2]ClO_4$  and  $[Rh_2(\mu-dipy)Cl(diolefin)_2]$ .

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,  $\alpha = 103.209(2)^\circ$ ,  $\beta = 110.278(2)^\circ$ , and  $\gamma = 88.125(2)^\circ$ , 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  $\beta$ -diketones, dipyrro-

methenes 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.

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

|       | Compound                                                                                                   | Colour      | Yield (%) | Analysis <sup>a</sup> |                |                  | Molecular weight <sup>a</sup> | Molar conductivity (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> ) |
|-------|------------------------------------------------------------------------------------------------------------|-------------|-----------|-----------------------|----------------|------------------|-------------------------------|---------------------------------------------------------------------------|
|       |                                                                                                            |             |           | C%                    | H%             | N%               |                               |                                                                           |
| I     | [Rh(cod)(Hdipy)]ClO <sub>4</sub> •Me <sub>2</sub> O                                                        | yellow      | 90        | 46.3<br>(46.72)       | 5.1<br>(5.04)  | 7.85<br>(7.78)   |                               | 109                                                                       |
| II    | [Rh(nbd)(Hdipy)]ClO <sub>4</sub>                                                                           | yellow      | 87        | 43.8<br>(43.84)       | 3.7<br>(3.68)  | 9.2<br>(9.02)    |                               | 108                                                                       |
| III   | [Rh(tfb)(Hdipy)]ClO <sub>4</sub>                                                                           | yellow      | 81        | 44.4<br>(44.06)       | 2.85<br>(2.52) | 7.0<br>(7.00)    |                               | 120                                                                       |
| IV    | [Ir(cod)(Hdipy)]ClO <sub>4</sub>                                                                           | yellow      | 81        | 37.5<br>(37.86)       | 3.7<br>(3.88)  | 7.6<br>(7.36)    |                               | 97                                                                        |
| V     | [Rh(CO) <sub>2</sub> (Hdipy)]ClO <sub>4</sub>                                                              | pale-yellow | 85        | 33.5<br>(33.55)       | 2.1<br>(2.11)  | 10.1<br>(9.78)   |                               | 130                                                                       |
| VII   | [Rh(dipy)(cod)]                                                                                            | yellow      | 89        | 56.5<br>(56.70)       | 5.3<br>(5.28)  | 11.1<br>(11.02)  | 406<br>(381)                  |                                                                           |
| VIII  | [Rh(dipy)(nbd)]                                                                                            | yellow      | 92        | 56.0<br>(55.90)       | 4.5<br>(4.41)  | 11.45<br>(11.50) | 344<br>(365)                  |                                                                           |
| IX    | [Rh(dipy)(tfb)]                                                                                            | yellow      | 85        | 52.2<br>(52.92)       | 2.7<br>(2.83)  | 8.5<br>(8.41)    | 540<br>(499)                  |                                                                           |
| X     | [Ir(dipy)(cod)]                                                                                            | yellow      | 88        | 45.6<br>(45.94)       | 4.2<br>(4.28)  | 9.0<br>(8.93)    | 990<br>(470)                  |                                                                           |
| XI    | [Ir(dipy)(tfb)]                                                                                            | yellow      | 75        | 44.5<br>(44.89)       | 2.1<br>(2.40)  | 7.3<br>(7.14)    | 630<br>(588)                  |                                                                           |
| XII   | [RhCl(nbd)(Hdipy)]                                                                                         | yellow      | 94        | 49.8<br>(50.82)       | 4.3<br>(4.26)  | 10.3<br>(10.46)  |                               |                                                                           |
| XIII  | [RhCl(tfb)(Hdipy)]                                                                                         | yellow      | 79        | 49.1<br>(49.32)       | 2.9<br>(2.82)  | 7.9<br>(7.84)    |                               |                                                                           |
| XIV   | [IrCl(cod)(Hdipy)]                                                                                         | yellow      | 77        | 42.1<br>(42.63)       | 3.8<br>(4.17)  | 8.4<br>(8.28)    | 645<br>(507)                  | 11                                                                        |
| XV    | [Rh(CO) <sub>2</sub> (Hdipy)][RhCl <sub>2</sub> (CO) <sub>2</sub> ]                                        | orange      | 80        | 30.1<br>(30.02)       | 1.6<br>(1.62)  | 7.4<br>(7.50)    |                               | 102                                                                       |
| XVI   | [Ir(CO) <sub>2</sub> (Hdipy)][IrCl <sub>2</sub> (CO) <sub>2</sub> ]                                        | green       | 79        | 22.8<br>(22.76)       | 1.3<br>(1.30)  | 5.8<br>(5.69)    |                               | 113                                                                       |
| XVII  | [(nbd)Rh(μ-dipy)Rh(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]-ClO <sub>4</sub> •CH <sub>2</sub> Cl <sub>2</sub> | yellow      | 66        | 54.0<br>(53.81)       | 3.8<br>(3.85)  | 3.3<br>(3.49)    |                               | 123                                                                       |
| XVIII | [(tfb)Rh(μ-dipy)Rh(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]-ClO <sub>4</sub>                                  | yellow      | 81        | 56.3<br>(56.50)       | 3.5<br>(3.54)  | 3.5<br>(3.35)    |                               | 118                                                                       |
| XIX   | [Rh <sub>2</sub> (μ-dipy)Cl(cod) <sub>2</sub> ]                                                            | yellow      | 67        | 49.3<br>(49.70)       | 5.3<br>(5.14)  | 6.8<br>(6.69)    | 626<br>(628)                  |                                                                           |
| XX    | [Rh <sub>2</sub> (μ-dipy)Cl(nbd) <sub>2</sub> ]                                                            | yellow      | 69        | 48.3<br>(48.31)       | 4.0<br>(4.05)  | 7.0<br>(7.04)    | 643<br>(597)                  |                                                                           |
| XXI   | [Rh <sub>2</sub> (μ-dipy)Cl(tfb) <sub>2</sub> ]                                                            | yellow      | 73        | 47.0<br>(47.27)       | 2.6<br>(2.33)  | 4.8<br>(4.86)    | 828<br>(864)                  |                                                                           |

<sup>a</sup>Found (calc.)%.

### Measurements

Elemental analyses (Table I) were carried out with a Perkin-Elmer 240 B microanalyzer. Infrared spectra (range 4000–200 cm<sup>-1</sup>) 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<sup>-4</sup> mol l<sup>-1</sup> acetone solutions using a Philips 9501/01 conductimeter. Molecular weights were determined in chloroform with a

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

### Syntheses

#### Preparation of $[\text{Rh}(\text{diolefin})(\text{Hdipy})]\text{ClO}_4$ (I–III) and $[\text{Ir}(\text{cod})(\text{Hdipy})]\text{ClO}_4$ (IV)

A solution of  $[\text{M}(\text{diolefin})(\text{OCMe}_2)_x]^+$  ( $\text{M} = \text{Rh}$ , diolefin = cod, nbd, tfb;  $\text{M} = \text{Ir}$ , diolefin = cod), prepared by reaction of the appropriate compound  $[\text{MCl}(\text{diolefin})]_2$  (0.1 mmol) with  $\text{AgClO}_4$  (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 $[\text{M}(\text{CO})_2(\text{Hdipy})]\text{ClO}_4$ ( $\text{M} = \text{Rh}$ (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 $[\text{M}(\text{dipy})(\text{diolefin})]$ ( $\text{M} = \text{Rh}$ , diolefin = cod (VII), nbd (VIII), tfb (IX); $\text{M} = \text{Ir}$ , 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 ( $1.4 \text{ mol l}^{-1}$  in hexane, 0.1 ml, 0.2 mmol) for 30 min to give a white suspension. The appropriate compound  $[\text{MCl}(\text{diolefin})]_2$  (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  $[\text{IrCl}(\text{tfb})_2]$  (68 mg, 0.1 mmol) and the reaction time was 12 h.

### Deprotonation and Protonation Reactions

#### (a) Reaction of the complexes of the type $[\text{Rh}(\text{diolefin})(\text{Hdipy})]\text{ClO}_4$ 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 ( $0.090 \text{ mol l}^{-1}$ , 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 $[\text{Rh}(\text{dipy})(\text{nbd})]$ with $\text{HBF}_4$

Tetrafluoroboric acid (50% in water, 12.5  $\mu\text{l}$ , 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  $[\text{Rh}(\text{nbd})(\text{Hdipy})]\text{BF}_4$ . Yield, 50%. Anal. Calc. for  $\text{C}_{17}\text{H}_{17}\text{N}_3\text{BF}_4\text{Rh}$ : C, 45.07; H, 3.78; N, 9.27. Found: C, 44.5; H, 3.9; N, 9.3%.

#### (c) Reactions of the complexes 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 ( $12 \text{ mol l}^{-1}$  in water, 8.4  $\mu\text{l}$ , 0.1 mmol) was added to give yellow solutions from which yellow solids precipitated 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 $[\text{MCl}(\text{diolefin})(\text{Hdipy})]$ ( $\text{M} = \text{Rh}$ , diolefin = nbd (XII), tfb (XIII); $\text{M} = \text{Ir}$ , diolefin = cod (XIV))

2,2'-Dipyridylamine (34.4 mg, 0.2 mmol) was stirred with suspensions of the complexes  $[\text{MCl}(\text{diolefin})]_2$  (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 $[\text{M}(\text{CO})_2(\text{Hdipy})][\text{MCl}_2(\text{CO})_2]$ ( $\text{M} = \text{Rh}$ (XV), Ir (XVI))

Through a suspension of the complex  $[\text{MCl}(\text{cod})]_2$  ( $\text{M} = \text{Rh}$ , 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 $[(\text{diolefin})\text{Rh}(\mu\text{-dipy})\text{Rh}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (diolefin = nbd (XVII), tfb (XVIII))

Solid  $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{OCMe}_2)]\text{ClO}_4$  (41 mg, 0.05 mmol) was added to a dichloromethane solution (10 ml) of the complex  $[\text{Rh}(\text{dipy})(\text{diolefin})]$  (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, $\theta(\text{Cu}) < 45$                                                                                               |
| Unit cell parameters                                         |                                                                                                                                       |
| $a$ (Å)                                                      | 12.3651(4)                                                                                                                            |
| $b$ (Å)                                                      | 12.4386(3)                                                                                                                            |
| $c$ (Å)                                                      | 10.0809(3)                                                                                                                            |
| $\alpha$ (°)                                                 | 103.209(2)                                                                                                                            |
| $\beta$ (°)                                                  | 110.278(2)                                                                                                                            |
| $\gamma$ (°)                                                 | 88.125(2)                                                                                                                             |
| Packing                                                      |                                                                                                                                       |
| $V$ (Å <sup>3</sup> )                                        | 1414.1(1)                                                                                                                             |
| $Z$                                                          | 4                                                                                                                                     |
| $D$ (g cm <sup>-3</sup> )                                    | 1.716                                                                                                                                 |
| $M$                                                          | 365.239                                                                                                                               |
| $F(000)$                                                     | 736                                                                                                                                   |
| Experimental data                                            |                                                                                                                                       |
| Radiation and technique                                      | Cu K $\alpha$ , PW1100 diffractometer<br>bisecting geometry                                                                           |
| Monochromator                                                | graphite oriented                                                                                                                     |
| Collection mode                                              | $\omega/2\theta$ , $\theta < 65$ , $1 \times 1$ det. apertures<br>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<br>variation                                                                                          |
| $\mu$ (cm <sup>-1</sup> ), max. min.<br>transmission factors | 99.313, 0.489–0.116                                                                                                                   |
| Solution and refinement                                      |                                                                                                                                       |
| Solution                                                     | XRAY76 [20], Vax11/750                                                                                                                |
| Refinement                                                   | least-squares on $F_s$ , observed re-<br>flexions 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<br>$\langle w\Delta^2 \rangle$ vs. $\langle F_o \rangle$ or $\langle \sin \theta / \lambda \rangle$ |
| Maximum thermal values<br>(Å <sup>2</sup> )                  |                                                                                                                                       |
| Final $F$ peaks                                              | $U_{22}$ (C34) = 0.160(8)                                                                                                             |
| Final $R$ , $R_w$                                            | 1.22 e Å <sup>-3</sup> near the Rh atoms<br>0.033, 0.039                                                                              |
| Atomic factors                                               | International Tables for X-ray<br>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)  |

(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.

#### Preparation of the complexes [Rh<sub>2</sub>( $\mu$ -dipy)Cl(di-olefin)]<sub>2</sub> (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)]<sub>2</sub> (0.05 mmol) in dichloromethane

## Results and Discussion

Addition of solutions of the cationic species  $[M(\text{diolefin})(\text{Me}_2\text{CO})_x]^+$  ( $M = \text{Rh}, \text{Ir}$ ) in acetone to 2,2'-dipyridylamine (Hdipy) in the same solvent gives the complexes of the type  $[M(\text{diolefin})(\text{Hdipy})]\text{ClO}_4$  ( $M = \text{Rh}$ ; diolefin = cycloocta-1,5-diene (cod) (**I**), norborna-2,5-diene (nbd) (**II**), tetrafluorobenzobarrelene (tfb) (**III**);  $M = \text{Ir}$ , 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  $1713\text{ cm}^{-1}$ ; it is also detected by elemental analyses. The infrared spectra of complexes **I–IV** show several bands associated to  $\nu(\text{N–H})$  in the  $3350\text{--}3100\text{ cm}^{-1}$  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  $^1\text{H}$  NMR spectrum of complex **II** in  $d_6$ -acetone consists of three multiplet resonances for both of the magnetically equivalent pyridyl rings between  $\delta$  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  $^1\text{H}$  NMR spectrum is consistent with a  $C_{2v}$  symmetry of the complex, as observed for the compound *trans*- $[\text{RuCl}_2(\text{bipy})(\text{nbd})]$  [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  $[\text{Rh}(\text{CO})_2(\text{Hdipy})]\text{ClO}_4$  (**V**) and  $[\text{Ir}(\text{CO})_2(\text{Hdipy})]\text{ClO}_4$  (**VI**) which show two strong  $\nu(\text{CO})$  bands at 2095, 2035 and 2085, 2020  $\text{cm}^{-1}$ , respectively; these bands are characteristic of a *cis*-dicarbonyl metal structure. Complex **V** is isolated as a yellow analytically pure solid, whereas  $[\text{Ir}(\text{CO})_2(\text{Hdipy})]\text{ClO}_4$  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  $\text{cm}^{-1}$ ) on the two strong bands. In the solid state (Nujol), the complex displays four  $\nu(\text{CO})$  bands at 2100vs, 2075s, 2020vs and 1990m  $\text{cm}^{-1}$ . The deep-blue colour and the splitting of the  $\nu(\text{CO})$  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]. Com-

plexes **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  $[\text{Rh}(\text{nbd})(\text{Hdipy})]\text{ClO}_4$  reacts with potassium hydroxide in methanol to give crude  $[\text{Rh}(\text{dipy})(\text{nbd})]$ . The general route to the complexes  $[M(\text{dipy})(\text{diolefin})]$  [ $M = \text{Rh}$ , diolefin = cod (**VII**), nbd (**VIII**), tfb (**IX**);  $M = \text{Ir}$ , diolefin = cod (**X**), tfb (**XI**)] consists of reacting the compounds  $[\text{MCl}(\text{diolefin})]_2$  or  $[\text{IrCl}(\text{tfb})]_2$  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  $\nu(\text{NH})$  in the  $3350\text{--}3100\text{ cm}^{-1}$  region. Their molecular weights in chloroform solution are those expected for mononuclear complexes, except for complex **X** which apparently is binuclear.

The  $^1\text{H}$  NMR spectrum of complex  $[\text{Rh}(\text{dipy})(\text{nbd})]$ , 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  $^1\text{H}$  NMR spectra (see Table IV).

The neutral complex  $[\text{Rh}(\text{dipy})(\text{nbd})]$  reacts with noncoordinating protonic acids such as tetrafluoroboric acid to regenerate the cationic complex  $[\text{Rh}(\text{nbd})(\text{Hdipy})]\text{BF}_4$ . Coordinating acids, such as hydrochloric acid, react with the neutral complexes **VIII** and **IX** to give yellow materials analysing as  $[\text{RhCl}(\text{nbd})(\text{Hdipy})]_x$  and  $[\text{RhCl}(\text{tfb})(\text{Hdipy})]_x$ , respectively. These compounds and  $[\text{IrCl}(\text{cod})(\text{Hdipy})]_x$  (**XIV**) can be prepared by reaction of the complexes  $[\text{RhCl}(\text{diolefin})]_2$  or  $[\text{IrCl}(\text{cod})]_2$  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  $\text{ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$  for  $6.1 \times 10^{-4}\text{ mol l}^{-1}$  solution\*\*). On the other hand, molecular weight measurements suggest  $x = 3$ .

The  $^1\text{H}$  NMR spectrum of this complex in  $\text{CDCl}_3$  shows intense resonances for a symmetrical species which is the most abundant in solution (given

\*Similar features are shown by the complexes  $[M(\text{CO})_2]_2$  ( $\text{C}_2\text{O}_4$ ) ( $M = \text{Rh}, \text{Ir}$ ) [23b].

\*\*Calculated for molecular weight = 507.

TABLE IV.  $^1\text{H}$  NMR Data for Selected Complexes<sup>a</sup>

| Compound    | Solvent               | Heterocyclic ring protons |                   |                    |                     | Diolefin                                                                                    |
|-------------|-----------------------|---------------------------|-------------------|--------------------|---------------------|---------------------------------------------------------------------------------------------|
|             |                       | H <sup>3/3'</sup>         | H <sup>4/4'</sup> | H <sup>5/5'</sup>  | H <sup>6/6'</sup>   |                                                                                             |
| <b>I</b>    | $\text{d}_6$ -acetone | 7.40dt <sup>b</sup>       | 8.00ddd           | 7.11ddd            | 7.37dt <sup>b</sup> | 4.34(q <sup>b</sup> , 4H, olefinic), 3.95(m, 2H, CH), 1.54(t, 1.70Hz, 2H, CH <sub>2</sub> ) |
| <b>VIII</b> | $\text{CDCl}_3$       | 7.07d                     | 7.32ddd           | 6.31ddd            | 6.75d               | 3.89(t <sup>b</sup> , 4H, olefinic), 3.83(m, 2H, CH), 1.55(t, 1.40Hz, 2H, CH <sub>2</sub> ) |
| <b>IX</b>   | $\text{CDCl}_3$       | 7.26d                     | 7.41ddd           | 6.35ddd            | 6.70d               | 5.54(m, 2H, CH), 3.73(m, 4H, olefinic)                                                      |
| <b>X</b>    | $\text{CDCl}_3$       | 7.11d                     | 7.37ddd           | 6.37ddd            | 7.70d               | 3.85(m, 4H, olefinic), 2.30(m, 4H, CH <sub>2</sub> ), 1.73m, 4H, CH <sub>2</sub> )          |
| <b>XI</b>   | $\text{CDCl}_3$       | 6.86d                     | 7.50m             | 6.38t <sup>b</sup> | 7.50m               | 5.48(m, 2H, CH), 2.96(m, 4H, olefinic)                                                      |
| <b>XIV</b>  | $\text{CDCl}_3$       | 8.18m                     | 7.69ddd           | 6.92ddd            | 8.09d               | 3.84(m, 4H, olefinic), 2.3(m, 4H, CH <sub>2</sub> ), 1.6(m, 4H, CH <sub>2</sub> )           |
| <b>XV</b>   | $\text{d}_6$ -acetone | 7.68d                     | 8.17ddd           | 7.36ddd            | 8.80d               |                                                                                             |

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

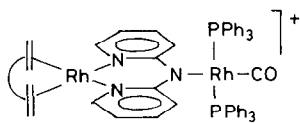
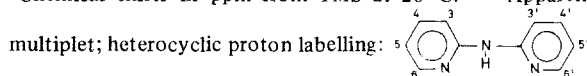


Fig. 1. Proposed structure for the species  $[(\text{diolefin})\text{Rh}(\mu\text{-dipy})\text{Rh}(\text{CO})(\text{PPh}_3)_2]^+$ .

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  $\nu(\text{CO})$  bands; they were not further investigated. On the other hand, if carbon monoxide is bubbled through a suspension of  $[\text{RhCl}(\text{cod})]_2$  or  $[\text{IrCl}(\text{cod})]_2$  and the ligand in dichloromethane in molar ratio 1:1, solutions of the complexes of the type  $[\text{M}(\text{CO})_2(\text{Hdipy})][\text{MCl}_2(\text{CO})_2]$  ( $\text{M} = \text{Rh}$  (**XV**),  $\text{Ir}$  (**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  $\nu(\text{CO})$  bands of the anion  $[\text{MCl}_2(\text{CO})_2]^-$  and those reported above for the cation at 2090, 2060, 2020, 1985  $\text{cm}^{-1}$  (complex **XV**) and 2080, 2045, 2000, 1965 (complex **XVI**) in the solid state. The  $^1\text{H}$  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  $[\text{Rh}(\text{dipy})(\text{diolefin})]$  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  $[(\text{diolefin})\text{Rh}(\mu\text{-dipy})\text{Rh}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$  (diolefin = nbd (**XVII**), tfb (**XVIII**)) are obtained by reaction of complexes **VIII** and **IX** with  $[\text{Rh}(\text{CO})(\text{PPh}_3)_2(\text{OCMe}_2)]\text{ClO}_4$  [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  $\nu(\text{CO})$  band at 1990 and 1995  $\text{cm}^{-1}$ , respectively, in dichloromethane.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **XVII** displays a resonance doublet at 34.7 ppm ( $J_{\text{RhP}}$ : 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  $[\text{Rh}(\text{dipy})(\text{diolefin})]$  produce bridge-cleavage reactions of the complexes  $[\text{RhCl}(\text{diolefin})]_2$  to give binuclear neutral complexes of the type  $[(\text{diolefin})\text{Rh}(\mu\text{-dipy})\text{RhCl}(\text{diolefin})]$  (**XIX–XXI**). They are air-stable solids and their molecular weights in solution are in accordance with the proposed formulae. Their  $^1\text{H}$  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  $[\text{M}(\text{dipy})(\text{diolefin})]$  and  $[\text{M}(\text{diolefin})\text{Hdipy}]\text{ClO}_4$  complexes ( $\text{M} = \text{Rh}$ , diolefin = cod, nbd;  $\text{M} = \text{Ir}$ , 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.

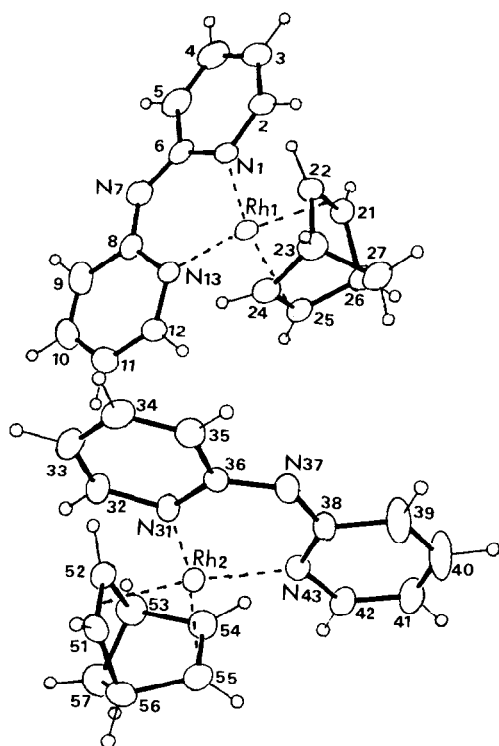


Fig. 2. View of the asymmetric unit showing the atomic numbering of  $[\text{Rh}(\text{dipy})(\text{nbd})]$ . Carbon symbols are omitted for clarity.

### Structure of $[\text{Rh}(\text{dipy})(\text{nbd})]$

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  $\text{Rh}(\text{nbd})$  moiety is remarkably narrower than  $90^\circ$ . The plane defined by the  $\text{RhN}_2$  entity and that defined by the Rh atom and the midpoint of the olefinic bonds form angles of  $2.8(1)$  and  $2.7(1)^\circ$  (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  $1.341 \text{ \AA}$ ); they are similar to those found in the related neutral complex  $[\text{Cu}(\text{dipy})_2]$  [27] and significantly shorter ( $4.8 \sigma_p$ ) than in the free Hdipy ligand and in the complexes  $\{[\text{CuI}(\text{Hdipy})_2]_2\}\text{I}(\text{ClO}_4)$  [28] and  $[\text{Cu}$

TABLE V. Selected Bond Distances ( $\text{\AA}$ ) and Bond Angles ( $^\circ$ )

|                            |           |                            |           |
|----------------------------|-----------|----------------------------|-----------|
| 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 <sup>a</sup> | 71.2(2)   | C512–Rh2–C545 <sup>a</sup> | 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)   |
| N1–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)  |

<sup>a</sup>C212, C245, C512 and C545 are the midpoints of the olefinic bonds.

$(\text{C}_2\text{H}_4)(\text{Hdipy})]\text{ClO}_4$  [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:  $\text{N}(\text{bridge})\text{--C--N} > \text{C--C--N} > \text{C--C--N}(\text{bridge})$ . 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 ( $\chi^2$  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,  $\phi_2 = 42(3)$ ,  $36(3)^\circ$  and  $\theta = 67(3)$ ,  $75(2)^\circ$ , respectively, compared with those of perfect diplanar boat conformations  $\theta_2 = 30$ ,  $60^\circ$  and  $\phi = 67.5$ ,  $90^\circ$ ).

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. Villarroja, 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. Crabtree, *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, '<sup>31</sup>P and <sup>13</sup>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. Schlatter, 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. Aprea, C. Foces-Foces, F. H. Cano and S. García-Blanco, *J. Organomet. Chem.*, 256, 331 (1983).