Inorganica Chimica Acta, *147* (1988) 243–250

Rhodium(III) *cis*-Dihydrido Complexes with 3,6-Bis(2′-pyridyl)pyridazine (dppn) and Bidiazines. Crystal and Molecular Structure of $[Rh(H)_2(dppn)(PPh_3)_2]PF_6 \cdot CH_2Cl_2$

MAURO GHEDINI, FRANCESCO NEVE

Dipartimento di Chimica, Universita' della Calabria, 87030 Arcavacata di Rende (CS), Italy

ANNA MARIA MANOTTI LANFREDI and FRANCO UGOZZOLI

Istituti di Chimica Generale ed Inorganica e di Strutturistica Chimica, Universita' di Parma, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Viale delle Scienze, 43100 Parma, Italy

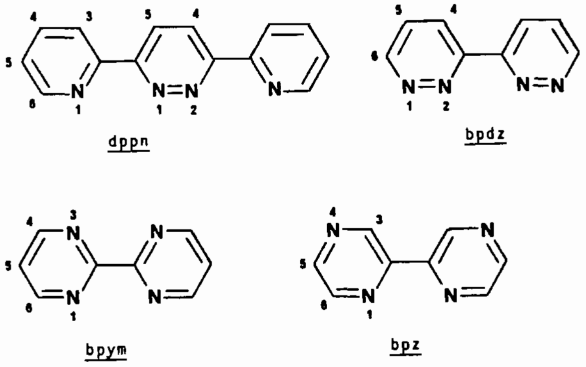
(Received November 19, 1987)

Abstract

The acetone complex $[Rh(H)_2(acetone)_2(PPh_3)_2]PF_6$ reacts with bidiazines and 3,6-bis(2′-pyridyl)pyridazine (dppn) giving the air stable *cis*-dihydrido rhodium(III) $[Rh(H)_2(L)(PPh_3)_2]PF_6$ complexes. The structure of the dichloromethane solvate of $[Rh(H)_2(dppn)(PPh_3)_2]PF_6$ has been determined by X-ray crystal structure analysis. Crystals are monoclinic, space group $P2_1/a$, with $a = 18.629(6)$, $b = 15.339(5)$, $c = 17.146(5)$ Å, $\beta = 101.02(3)°$ and $Z = 4$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by block-matrix least-squares to $R = 0.076$ for 6225 observed reflections. In the structure discrete $[Rh(H)_2(dppn)(PPh_3)_2]^+$ cationic complexes, PF_6^- anions and dichloromethane solvent molecules are present. The Rh atom is octahedrally surrounded by two *cis* hydride ligands and by two *cis* nitrogen atoms from a dppn molecule acting as a bidentate chelating ligand through two neighbouring pyridyl and pyridazinyl nitrogen atoms. Two P atoms from PPh_3 ligands in *trans* apical positions complete to octahedral the coordination of Rh.

Introduction

The chelate ligands of the 2,2′-bipyridine (bipy) family are the subject of several recent studies [1, 2]. In this field we are currently concerned with the study of the coordination chemistry of the tetradentate ligand 3,6-bis(2′-pyridyl)pyridazine (dppn), from which either binuclear or mononuclear complexes can be obtained [3–6]. In the former, dppn displays a bis-chelating coordination, with the two metal centers held in a side-by-side arrangement, while in the latter, where two neighbouring pyridinic and pyridazinic nitrogen atoms are involved in the coordination, dppn behaves as a trinitrogenate 2,2′-bipyridine-like ligand. As the incorporation of a further nitrogen center into a bipy skeleton leads to a more π-electron-deficient ligand [7–9], we have investigated the cationic mononuclear *cis*-dihydrido bis-triphenylphosphine rhodium(III) complexes containing dppn and bidiazines, with a view of a greater understanding of the dppn ligand.



Scheme 1.

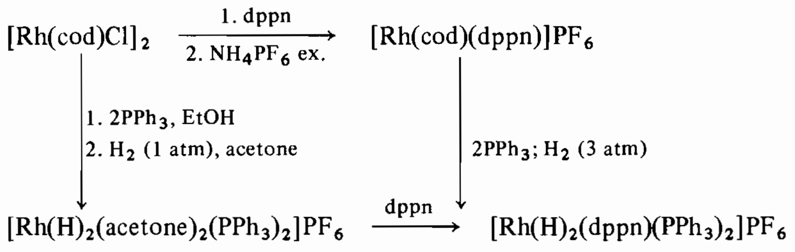
In this paper we report the synthesis and characterization of the complexes $[Rh(H)_2(L)(PPh_3)_2]PF_6$, were L is one of the following ligands: dppn; 3,3′-bipyridazine (bpdz); 2,2′-bipyrimidine (bpym) and 2,2′-bipyrazine (bpz) (Scheme 1). The similar cationic complex $[Rh(H)_2(bipy)(PPh_3)_2]^+$ is known from the literature [10–12].

The X-ray analysis of the complex $[Rh(H)_2(dppn)(PPh_3)_2]PF_6$, one of the few examples of octahedral *cis*-dihydrido rhodium(III) complexes structurally characterized [13–16], is also reported.

Results and Discussion

Synthesis of $[Rh(H)_2(dppn)(PPh_3)_2]PF_6$ (2)

The known cationic complex $[Rh(H)_2(bipy)(PPh_3)_2]^+$ was synthesized by other authors following three different routes, namely: (a) oxidative addition



Scheme 2. Preparation of $[Rh(H)_2(dppn)(PPh_3)_2]PF_6$.

TABLE I. ^{1}H and ^{31}P{^{1}H} NMR Data for the Rh(III) *cis*-Dihydrido Complexes 2–5

Complex	Rh–H			δ(P) (ppm)
	δ(H) (ppm)	^2J(PH) (Hz)	^1J(RhH) (Hz)	
$[Rh(H)_2(bipy)(PPh_3)_2]PF_6$[a, b]	−15.66	14.5	14.5	
2[b]	−14.91[c]	13.5	13.5	44.31[d]
	−15.65[c]	13.5	13.5	
3[e]	−14.90	13.4	13.4	46.10[f]
4[e]	−15.21	13.4–14.0	13.4–14.0	47.30[g]
5[e]	−15.49	13.4–14.0	13.4–14.0	47.94[h]

[a]From ref. 12. [b]In CD_2Cl_2 at 20 °C. [c]^2J(HH) = 13.5 Hz. [d]^1J(RhP) = 117.2 Hz. [e]In $(CD_3)_2CO$ at 20 °C. [f]^1J(RhP) = 117.2 Hz. [g]^1J(RhP) = 114.8 Hz. [h]^1J(RhP) = 114.8 Hz.

of H_2 on $[Rh(cod)(bipy)]^+$ in presence of PPh_3 [10]; (b) reduction of $[Rh(bipy)_2Cl_2]^+$ with $NaBH_4$ and addition of PPh_3 [11] and (c) displacement with bipy of the coordinate solvent (S) in $[Rh(H)_2(S)_2(PPh_3)_2]^+$ [12].

Comparing the reaction schemes (a)–(c) we discarded the route (b) to avoid ligand wastage, therefore the preparation of complex 2 was performed according to Scheme 2.

The dimer $[Rh(cod)Cl]_2$ reacts quantiatively with dppn, and then with NH_4PF_6, affording the new complex $[Rh(cod)(dppn)]PF_6$ (1) which was characterized by elemental analysis, conductivity measurements, IR and ^{1}H NMR spectroscopy (see 'Experimental'). The subsequent addition of H_2 to 1 in the presence of PPh_3 gives rise to product 2 (68% yield). Alternatively, 2 can be obtained in higher yield (98%) by stoichiometric addition of dppn on the known solvento complex $[Rh(H)_2(acetone)_2(PPh_3)_2]PF_6$ [12].

Complex 2 has been characterized by elemental analysis, conductivity measurements and spectral methods (see Table I and 'Experimental'). In particular, the single resonance in the ^{31}P{^{1}H} NMR spectrum of 2 (δ 44.31, ^1J(RhP) = 117.2 Hz) indicates equivalence of two phosphines mutually *trans*.

Moreover, the ^{1}H NMR spectrum of 2 in CD_2Cl_2 at 20 °C exhibits two hydrido signals at δ − 14.91 and −15.65, both as quintets (1:4:6:4:1) of equal intensity. They both arise from a pair of overlapping quartets (1:3:3:1) because the coupling constants are essentially equal (^1J(RhH) = ^2J(PH) = ^2J(HH) = 13.5 Hz). The coincidence of the coupling constants has been also found in other hydrido phosphino complexes of rhodium(III) [11, 17]. The value of ^2J(PH) also suggests that the PPh_3 groups are *cis* to non-equivalent hydrogen atoms.

Crystal Structure of $[Rh(H)_2(dppn)(PPh_3)_2]PF_6 \cdot CH_2Cl_2$

Crystals of 2 suitable for X-ray analysis were obtained from CH_2Cl_2:Et_2O solution. The crystal structure consists of discrete $[Rh(H)_2(dppn)(PPh_3)_2]^+$ cations, PF_6^- counterions and CH_2Cl_2 solvent molecules. A view of the cationic complex with the atomic numbering scheme is given in Fig. 1; relevant bond distances and angles are given in Table II.

The Rh atom is octahedrally surrounded by two *trans* apical PPh_3 groups, by two *cis* hydrido ligands and by two *cis* nitrogen atoms from a dppn molecule acting as a bidentate chelating ligand through two neighbouring pyridyl and pyridazinyl nitrogens. The two non-coordinating N atoms (one from the pyridazine moiety and one from the other pyridyl ring) are mutually *trans* so the conformation of the organic ligand is the same as that found in the mononuclear cation $[Cu(dppn)_2Cl]^+$ [18]. The same conformation has been also observed in the deprotonated dppn ligand in the structure of the dinuclear cationic complex $\{[Ir(H)_2(PPh_3)_2]_2[\mu\text{-}C_4HN_2\text{-}3,6(C_5H_4N)_2]\}^+$ [19]. In this

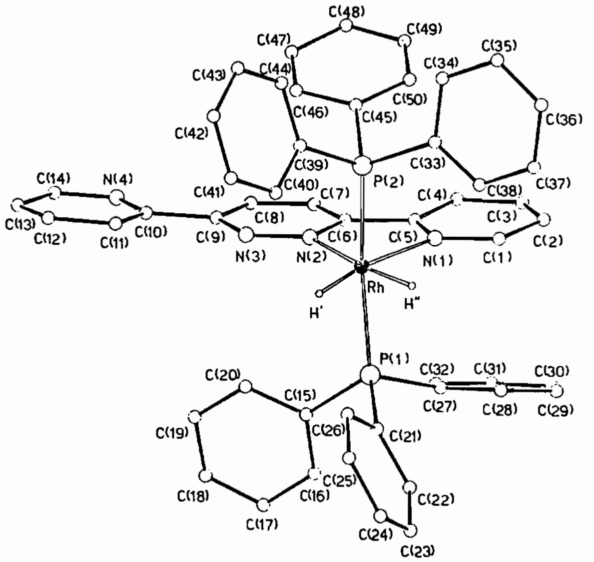


Fig. 1. View of the cationic complex $[Rh(H)_2(dppn)(PPh_3)_2]^+$ with the atomic numbering scheme.

last case the deprotonated dppn, acting as a tetradentate ligand, chelates on opposite sides two metal atoms, the former through one pyridyl and one pyridazinyl nitrogen atom, the latter through one pyridyl nitrogen and one pyridazinyl carbon atom. Different conformation of the neutral dppn, with pyridyl nitrogen atoms on the same side with respect to the N–N bond of the pyridazinyl ring, allows the chelation on the same side and through the four nitrogen atoms, of two metal atoms in the homodinuclear $[Cu_2(dppn)Cl_3(OH)(OH_2)]$ complex [20] and in the mixed metal cation $[IrCl(PPh_3)_2(dppn)(NO)CuCl]^{2+}$ [3]. The Rh–N bond lengths of 2.110(6) and 2.132(6) Å are longer than the mutually *trans* Rh(III)–nitrogen bond distances found in the octahedral cations $[Rh(NCMe)_3(NO)(PPh_3)_2]$ (2.030 and 2.014 Å) [21] and $[RhH(NH_3)_5]^+$ (2.086 and 2.071 Å, 2.048 and 2.079 Å) [23]. This lengthening may result from the influence of the two *trans* hydrido ligands.

The hydrido ligands were detected in a Fourier difference map although their refinement did not give good results. On the other hand, from our results (Rh–H′ = 1.46 and Rh–H″ = 1.61 Å, H′–Rh–H″ = 78.1°), the average value (1.53 Å) of the found Rh(III)–hydride distances is close to the values ranging from 1.5 to 1.7 Å found previously for terminal metal–hydride bonds [23] and comparable to the value (1.52 Å av.) found in complexes containing octahedral dihydride Rh(III) moieties [14, 16]. In these last compounds the terminal *cis* hydrides are *trans* to hydride or chloride bridges connecting R(III) and Rh(I) metal atoms. In the mononuclear Rh(III) complex, $[RhH_2(O_2COH)(PPr^i_3)_2]$ [13], the average value of the *cis* Rh–H bond lengths, *trans* to oxygen atoms, is 1.44(5) Å. To the best of our knowledge, octahedral Rh(III) complexes containing *cis* hydride ligands, *trans* to nitrogen atoms, are unknown. In the octahedral $[RhH(NH_3)_5]^{2+}$ cation [22], only one H ligand, exerting a pronounced *trans* effect on one amine group, is present. The distance between H′ and H″ is 1.94 Å and the narrow angle H′–Rh–H″ of 78.1°, may be compared with those found in the dinuclear $H_4Rh_2\{P[N(CH_3)_2]_3\}_4$ [14] (74(2)°) and $Rh_2H_2(O_2CO)(PhC{=}CPh)(PPr^i_3)_3$ [15] (73(2)°) complexes and in the mononuclear $[RhH_2(O_2COH)(PPr^i_3)_2]$ [13] complex (81°).

The *trans* axial Rh–P distances (av. 2.308(2) Å) are normal for octahedral Rh(III) complexes [13–15] and shorter than those observed (2.362(3) and 2.366(3) Å) in the *cis* dihydride $RhCl(H)_2(PBu^t_3)_2$ [24] complex, containing *trans* apical phosphine

TABLE II. Relevant Bond Distances (Å) and Angles (°)

Rh–P1	2.300(2)	N4–C10	1.330(11)
Rh–P2	2.317(2)	N4–C14	1.305(12)
Rh–N1	2.132(6)	C1–C2	1.380(13)
Rh–N2	2.110(6)	C2–C3	1.323(14)
P1–C15	1.817(9)	C3–C4	1.383(16)
P1–C21	1.818(6)	C4–C5	1.386(12)
P1–C27	1.806(7)	C5–C6	1.473(11)
P2–C33	1.835(9)	C6–C7	1.381(12)
P2–C39	1.831(8)	C7–C8	1.324(13)
P2–C45	1.822(7)	C8–C9	1.414(11)
N1–C1	1.356(11)	C9–C10	1.471(11)
N1–C5	1.326(10)	C10–C11	1.329(14)
N2–N3	1.342(8)	C11–C12	1.423(16)
N2–C6	1.352(10)	C12–C13	1.354(16)
N3–C9	1.300(10)	C13–C14	1.435(16)
N1–Rh–N2	76.5(2)	N2–N3–C9	120.7(6)
P2–Rh–N2	93.6(2)	C10–N4–C14	118.7(9)
P2–Rh–N1	90.3(2)	N1–C1–C2	121.4(8)
P1–Rh–N2	99.0(2)	C1–C2–C3	119.1(9)
P1–Rh–N1	94.8(2)	C2–C3–C4	121.2(9)
P1–Rh–P2	167.2(1)	C3–C4–C5	117.3(9)
Rh–P1–C27	108.9(2)	N1–C5–C4	122.1(8)
Rh–P1–C21	116.8(2)	C4–C5–C6	121.3(8)
Rh–P1–C15	119.5(3)	N1–C5–C6	116.5(7)
C21–P1–C27	106.5(3)	N2–C6–C5	114.5(7)
C15–P1–C27	103.9(3)	C5–C6–C7	125.9(7)
C15–P1–C21	99.8(3)	N2–C6–C7	119.5(7)
Rh–P2–C45	110.1(2)	C6–C7–C8	120.0(7)
Rh–P2–C39	118.6(3)	C7–C8–C9	118.5(8)
Rh–P2–C33	117.1(3)	N3–C9–C8	120.7(7)
C39–P2–C45	105.1(3)	C8–C9–C10	122.3(7)
C33–P2–C45	103.4(4)	N3–C9–C10	116.9(7)
C33–P2–C39	100.9(4)	N4–C10–C9	115.9(8)
Rh–N1–C5	115.8(5)	C9–C10–C11	120.7(8)
Rh–N1–C1	125.7(6)	N4–C10–C11	123.4(8)
C1–N1–C5	118.5(7)	C10–C11–C12	120.5(10)
Rh–N2–C6	116.5(5)	C11–C12–C13	116.2(11)
Rh–N2–N3	123.2(5)	C12–C13–C14	119.3(9)
N3–N2–C6	120.3(6)	N4–C14–C13	121.7(9)

ligands in a bipyramidal trigonal arrangement. The P(1)–Rh–P(2) bond angle is 167.2(1)° with the Rh–P vectors bent toward the H′RhH″ plane, the Rh–P(1) and Rh–P(2) bonds forming with this plane, angles of 77.6° and 83.7° respectively. Similar situations have been found in previously mentioned *cis*-dihydride *trans*-phosphine Rh(III) complexes [13–15, 24] where the P–Rh–P angles are in the range 154.8–170.7°.

The dppn ligand is not planar but each individual ring is planar. The two pyridyl rings are twisted with respect to the pyridazine moiety, about the corrresponding exocyclic C–C bond, by the same angle (4.7(3)°). These twist angles are larger than those found for the binucleating dppn ligand in the above mentioned complexes [19, 20, 3] (where all atoms of the organic ligand are nearly coplanar) and almost narrower than those observed for the two mononucleating dppn molecules in the $[Cu(dppn)_2Cl]^+$ cation [18]. In this last compound the larger twist angles (8.5°) due to steric hindrance are found for the coordinated pyridyl group of both dppn ligands.

The bond distances and angles in the organic ligand agree with those reported for dppn in the mononuclear and dinuclear dppn complexes [18–20, 3], the greater differences being relative to the diiridium complex [19], where the ligand must be disordered with a pyridazine atom statistically bonded to two metal atoms.

The values of the C–C bond distances in the triphenylphosphine phenyl rings are in the range 1.34(2)–1.42(1) Å.

The values of the P–F bond distances and of the F–P–F angles, involving *cis* F atoms, are in the ranges 1.50(1)–1.59(1) Å and 83.9(5)–93.8(6)° respectively, suggesting the PF_6^- anion is quite regular. It should be noted that the fluorine atoms from the PF_6^- anion are involved in secondary interactions. The most significant involve a hydrogen atom of one dichloromethane molecule [C(512)...F(1) = 3.27(2), H(512)...F(1) = 2.25 Å, C(51)–H(512)–F(1) = 157.2°] and a phenyl hydrogen of the cationic complex [C(4)...F(5^i) ($i = 1/2 + x$, $1/2 - y$, z) = 3.17(2), H(4)...F(5^i) = 2.04 Å, C(4)–H(4)–F(5^i) = 165.9°] contributing, in a significative way, to the packing of the different species.

Synthesis of $[Rh(H)_2(L)(PPh_3)_2]PF_6$*; 3: L = bpdz; 4: L = bpz; 5: L = bpym*

The highest yield preparation of 2 was performed starting from the solvento complex $[Rh(H)_2(acetone)_2(PPh_3)_2]PF_6$, therefore compounds 3–5 were prepared in the same way. The new complexes, yellow or orange solids, were obtained in good yields (70–80%) and characterized by elemental analysis, conductivity measurements, IR and NMR spectroscopy (see Table I and 'Experimental'). The IR spectra show a broad absorption or two different bands in the region of Rh–H stretching according to a *cis*-dihydrido moiety, while the $^{31}P\{^1H\}$ NMR data indicate the equivalence of two PPh_3 mutually *trans*.

The ^1H NMR spectra of **3–5**, acetone-d_6 at 20 °C, in he hydrido region show a single resonance. In all cases the signal is a quartet (1:3:3:1) resulting from a pair of overlapping triplets (1:2:1) because $^1J(RhH) \simeq {}^2J(PH)$.

The geometry of the isoelectronic complexes 3–5, as shown above for 2, is suggested as octahedral, with the chelating ligand and the two *cis* hydrido groups on the equatorial plane, the two PPh_3 in the apical positions.

Conclusions

All the ligands in Scheme 1 react with the solvento complex $[Rh(H)_2(acetone)_2(PPh_3)_2]PF_6$ affording the compounds 2–5 in good yields.

The molecular structure of the dichloromethane solvate of 2 has been determined by X-ray analysis and the *cis* geometry of the two hydrido ligands lying on the dppn plane has been confirmed. Complexes 2–5 are isoelectronic, so that 3–5 are suggested to have the same structure as 2.

To the best of our knowledge, the dihydrides 3–5 are the first reported examples of octahedral dihydrides complexes containing bidiazine ligands. Therefore in the present case the chemical shifts of the hydrido ligands might be used as a further probe to investigate the electronic properties of such symmetrical chelate ligands. Thus, for the hydrido iridium(III) species *trans* $H(L)Ir(CO)(Cl)(PPh_3)_2$, Olgemöller and Beck reported that with decreasing the σ-donor strength of the *trans* ligand L, high-field shift of δ(IrH) occurred [25]. In the $[Rh(H)_2(L)(PPh_3)_2]PF_6$ complexes the highest field value of δ(RhH) is found at −15.49 ppm (5: L = bpym), while the lowest value is displayed by 3 at −14.90 ppm (L = bdpz). For the similar complex $[Rh(H)_2(bipy)(PPh_3)_2]PF_6$, Schrock and Osborn reported δ(RhH) = −15.66 ppm in dichloromethane solution [12]. Therefore, on the grounds of these data, which concern the set of bidiazines, it seems reasonable to conclude that the hydrido ligands experience the strongest *trans* influence following the order bpdz > bpz > bpym > bipy.

In the ^1H NMR spectrum of 2, which contains the asymmetrical chelate ligand dppn, two different signals are observed at −14.91 and −15.65 ppm. This evidence confirms the sensitivity of the ^1H NMR chemical shift of the hydride ligand on the donor group in *trans* position.

Therefore the comparison among the above reported data allows the attribution of the two signals, namely H′ at −15.65 ppm and H″ at −14.91 ppm.

Moreover the X-ray molecular structure of 2 shows Rh–H′ and Rh–H″ distances of 1.46 and 1.61 Å respectively, hence it seems noteworthy that the highest field value is found for the shortest Rh–H bond length and vice versa.

Finally, the complexes 2–5 are very stable toward dihydrogen elimination either as solids or in organic solvents such as acetone or dichloromethane. Complex 2 reacted with CO (2–3 atm) for several hours gives a mixture containing 2 as the main product. Interestingly, the IR spectrum of this mixture, KBr disc, shows bands at 2095w [ν(RhH)] and 2000s [ν(CO)] cm^{-1} probably attributable to a new hydrido carbonyl derivative.

Experimental

Apparatus and Techniques

All reactions were carried out in an atmosphere of oxygen-free dry nitrogen. Solvents were dried, deaerated and distilled under nitrogen prior to use. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WH 300 spectrometer; chemical shifts, δ (ppm), are relative respectively to Me_4Si (internal standard) and to 85% phosphoric acid (external) and the high-frequency-positive convention is used. Infrared spectra were recorded for KBr pellets on a Perkin-Elmer 1330 spectrophotometer. Conductivity measurements were performed using a LKB 5300 B Conductolyser conductivity bridge. The melting points are uncorrected. Elemental analyses were carried out by the Microanalysis Laboratory of the Istituto di Farmacia dell'Universita' di Pisa, Italy.

Reagents

2,2′-Bipyrimidine was purchased from Aldrich. The ligands 3,6-bis(2′-pyridyl)pyridazine [26], 3,3′-bipyridazine [27] and 2,2′-bipyrazine [28] were prepared by literature methods, as were the complexes $[Rh(cod)Cl]_2$ [29] and $[Rh(H)_2(acetone)_2(PPh_3)_2]PF_6$ [30].

Preparation of Compounds

$[Rh(\eta^4\text{-}C_8H_{12})(dppn)]PF_6$ (1)

$[Rh(cod)Cl]_2$ (0.5 g, 1.01 mmol) and dppn (0.7 g, 3.03 mmol) were dissolved in methanol (30 cm^3) to give a deep red solution. On addition of an excess of NH_4PF_6 (1.65 g, 10.1 mmol) dissolved in water (5 cm^3) to this solution a green precipitate was obtained immediately. It was filtered, washed with water, diethyl ether and vacuum dried (1.1 g, 92%), melting point (m.p.) 234 °C (decomp.). *Anal.* Found: C, 45.12; H, 3.37; N, 9.97. Calc. for $C_{22}H_{22}F_6N_4PRh$: C, 44.76; H, 3.76; N, 9.49%. Molar conductivity: $\Lambda_M = 75.70$ Ω^{-1} mol^{-1} cm^2 (10^{-3} mol dm^{-3}) in nitromethane. NMR data: δ_H (300 MHz, CD_2Cl_2, standard Me_4Si) 2.28 (4H, m, CH_2(cod)), 2.65 (4H, m, CH_2(cod)), 4.76 (2H, m, CH(cod)), 5.02 (2H, m, CH(cod)), 7.94 (1H, d, 6-pyH), 7.76 (1H, m, 5-pyH), 8.37–8.28 (3H, m, 4-pyH, 3-pyH, 3′-pyH), 8.79 (1H, ddd, $J_{6'5'} = 4.6$, $J_{6'4'} = 1.8$, $J_{6'3'} = 1.0$ Hz, 6′pyH), 7.52 (1H, ddd, $J_{5'4'} = 7.8$, $J_{5'3'} = 1.0$ Hz, 5′-pyH), 7.93 (1H, ddd, $J_{4'3'} = 7.8$ Hz, 4′-pyH), 8.54 (1H, d, $J_{54} = 9.0$ Hz, 5-pyridinazineH, 9.04 (1H, d, 4-pyridinazineH).

$[Rh(H)_2(dppn)(PPh_3)_2]PF_6$ (2)

(a) Oxidative addition of hydrogen to 1. A 100 cm^3 glass pressure-reaction bottle was charged with 1 (0.2 g, 0.34 mmol), triphenylphosphine (0.18 g, 0.68 mmol) and acetone (20 cm^3). Storage of the resulting red–brown solution under 3 atm of molecular hydrogen at room temperature for 24 h gave a yellow–orange solution. Then the pressure was released, diethyl ether (*ca.* 50 cm^3) was added, the mixture was cooled to –20 °C and allowed to stand overnight. The yellow–brown microcrystals of product were separated by filtration and vacuum dried (0.229 g, 68%), m.p. 149–151 °C. *Anal.* Found: C, 56.02; H, 3.92; N, 5.09. Calc. for $C_{50}H_{42}F_6N_4P_3Rh\cdot CH_2Cl_2$: C, 56.06; H, 4.06; N, 5.13%. Molar conductivity: $\Lambda_M = 71.80$ Ω^{-1} mol^{-1} cm^2 (10^{-3} mol dm^{-3}) in nitromethane.

IR (KBr disc): ν(Rh–H) 2100 and 2070 cm^{-1}. NMR data: δ_H (300 MHz, CD_2Cl_2, standard Me_4Si) 8.08 (1H, brd, $J_{65} = 5.2$ Hz, 6-pyH), 6.93 (1H, ddd, $J_{54} = 7.0$, $J_{53} = 1.9$ Hz, 5-pyH), 7.80 (1H, ddd; $J_{43} = 8.0$, $J_{64} = 1.6$ Hz, 4-pyH), 7.85 (1H, brd, 3-pyH), 8.76 (1H, ddd, $J_{6'5'} = 4.8$, $J_{6'4'} = 1.8$, $J_{6'3'} = 1.0$ Hz, 6′-pyH), 7.54 (1H, ddd, $J_{5'4'} = 7.6$, $J_{5'3'} = 1.0$ Hz, 5′-pyH), 8.05 (1H, ddd, $J_{4'3'} = 8.0$ Hz, 4′-pyH), 8.57 (1H, ddd, 3′-pyH), 7.99 (1H, d, $J_{54} = 9.0$ Hz, 5-pyridazineH), 8.56 (1H, d, 4-pyridazineH).

(b) Displacement reaction. A solution of dppn (0.04 g, 0.17 mmol) in CH_2Cl_2 (3 cm^3) was added to a stirred solution of $[Rh(H)_2(acetone)_2(PPh_3)_2]PF_6$ (0.15 g, 0.17 mmol) in CH_2Cl_2 (2 cm^3). The solution turned from pale yellow to yellow–brown and slow addition of diethyl ether resulted in the precipitation of a pale yellow solid, which was recrystallized from CH_2Cl_2–Et_2O giving yellow–brown crystals of 2 (0.15 g, 89%).

$[Rh(H)_2(bpdz)(PPh_3)_2]PF_6$ (3)

To a solution of bpdz (0.018 g, 0.11 mmol) in CHI_2Cl_2 (3 cm^3) was added a solution of $[Rh(H)_2(acetone)_2(PPh_3)_2]PF_6$ (0.1 g, 0.11 mmol) in CH_2Cl_2 (5 cm^3) and the resulting yellow–brown solution stirred at room temperature for 30 min. Slow addition of diethyl ether yielded yellow needles which were filtered off and vacuum dried (0.081 g, 78%),

TABLE III. Fractional Atomic Coordinates (×10^4) for the Non-hydrogen Atoms[a]

Atom	*x/a*	*y/b*	*z/c*
Rh	2682(1)	652(1)	2500(1)
P1	2383(1)	832(1)	1145(1)
P2	2793(1)	716(1)	3868(1)
P3	4108(2)	5708(2)	2311(2)
N1	2231(3)	−626(4)	2490(4)
N2	3600(3)	−168(4)	2557(3)
N3	4287(3)	133(4)	2640(4)
N4	6116(4)	−568(5)	2772(5)
C1	1517(5)	−818(6)	2469(5)
C2	1276(5)	−1669(6)	2461(6)
C3	1748(6)	−2309(6)	2441(8)
C4	2485(6)	−2142(6)	2491(6)
C5	2698(4)	−1277(5)	2484(4)
C6	3467(4)	−1035(5)	2509(4)
C7	4036(5)	−1606(5)	2487(6)
C8	4712(5)	−1307(5)	2556(6)
C9	4832(4)	−400(5)	2653(5)
C10	5569(4)	−16(6)	2791(5)
C11	5664(6)	834(7)	2922(8)
C12	6379(6)	1201(8)	3065(9)
C13	6934(5)	648(7)	3011(7)
C14	6782(5)	−264(8)	2886(6)
C15	3102(4)	832(4)	563(5)
C16	2957(5)	717(5)	−252(5)
C17	3513(6)	783(6)	−687(6)
C18	4210(6)	925(7)	−301(7)
C19	4382(5)	1037(7)	508(7)
C20	3823(4)	998(6)	941(6)
C21	1916(4)	1837(4)	787(4)
C22	1442(4)	1858(5)	46(5)
C23	1134(5)	2648(6)	−239(6)
C24	1281(5)	3401(6)	190(6)
C25	1746(6)	3372(6)	921(6)
C26	2064(5)	2586(5)	1221(5)
C27	1790(4)	−50(5)	726(4)
C28	1050(4)	−19(6)	753(5)
C29	613(5)	−751(6)	530(6)
C30	906(7)	−1507(7)	322(6)
C31	1644(7)	−1540(6)	303(6)
C32	2085(5)	−814(5)	503(6)
C33	1943(4)	747(5)	4260(5)
C34	1984(7)	597(7)	5059(7)
C35	1340(9)	627(7)	5358(9)
C36	698(7)	813(7)	4861(10)
C37	655(6)	963(9)	4076(8)
C38	1295(5)	907(7)	3776(7)
C39	3293(4)	1631(5)	4403(5)
C40	3284(6)	2407(6)	4021(7)
C41	3624(7)	3141(7)	4437(8)
C42	3943(5)	3060(7)	5223(7)
C43	3954(6)	2280(8)	5605(7)
C44	3623(5)	1564(7)	5195(6)
C45	3253(4)	−258(5)	4324(4)
C46	4005(5)	−301(7)	4450(6)
C47	4355(6)	−1085(8)	4685(7)
C48	3950(8)	−1799(8)	4835(8)
C49	3215(8)	−1762(7)	4687(8)
C50	2866(6)	−992(6)	4453(6)
F1	4877(5)	5247(6)	2333(6)
F2	4405(4)	6489(5)	1878(5)
F3	3866(5)	5223(6)	1516(6)
F4	3869(5)	4926(6)	2778(5)
F5	3388(7)	6166(9)	2236(7)
F6	4404(6)	6243(7)	3073(6)
Cl1	5363(2)	2944(3)	1700(2)
Cl2	4227(3)	2751(3)	2563(3)
C51	4498(8)	3236(9)	1779(8)

[a] e.s.d.s given in parentheses.

m.p. 158–160 °C. *Anal.* Found: C, 55.68; H, 4.00; N, 5.91. Calc. for $C_{44}H_{38}F_6N_4P_3Rh \cdot 0.2CH_2Cl_2$: C, 55.90; H, 4.07; N, 5.90%. Molar conductivity: $\Lambda_M = 81.20\ \Omega^{-1}\ mol^{-1}\ cm^2$ (10^{-3} mol dm^{-3}) in nitromethane. IR (KBr disc): ν(Rh–H) 2075br cm^{-1}. NMR data: δ_H (300 MHz, $(CD_3)_2CO$, standard Me_4Si) 9.04 (2H, d, $J_{65} = 6.0$ Hz, 6-pdzH), 7.90 (2H, dd, $J_{45} = 8.9$ Hz, 5-pdzH), 8.40 (2H, d, 4-pdzH).

[Rh(H)$_2$(bpz)(PPh$_3$)$_2$]PF$_6$ (4)

A solution of $[Rh(H)_2(acetone)_2(PPh_3)_2]PF_6$ (0.1 g, 0.11 mmol) in CH_2Cl_2 (5 cm^3) was added to a stirred solution of bpz (0.018 g, 0.11 mmol) in CH_2Cl_2 (2 cm^3). The solution turned to red–orange. After 30 min of stirring diethyl ether was slowly added until a pale yellow solid precipitated. This was crystallized from CH_2Cl_2–Et_2O (0.084 g, 80%), m.p. 155 °C (decomp.) *Anal.* Found: C, 55.07; H, 4.00; N, 5.77. Calc. for $C_{44}H_{38}F_6N_4P_3Rh \cdot 0.5CH_2Cl_2$: C, 54.81; H, 4.03; N, 5.74%. Molar conductivity: $\Lambda_M = 76.00\ \Omega^{-1}\ mol^{-1}\ cm^2$ (10^{-3} mol dm^{-3}) in nitromethane. IR (KBr disc): ν(Rh–H) 2070 and 2038 cm^{-1}. NMR data: δ_H (300 MHz, $(CD_3)_2CO$, standard Me_4Si) 8.49 (2H, brd, 6-pzH), 8.31 (2H, d, $J_{65} = 3.0$ Hz, 5-pzH), 9.63 (2H, s, 3-pzH).

[Rh(H)$_2$(bpym)(PPh$_3$)$_2$]PF$_6$ (5)

A solution of $[Rh(H)_2(acetone)_2(PPh_3)_2]PF_6$ (0.06 g, 0.067 mmol) in CH_2Cl_2 (3 cm^3) was added to a solution of bpym in CH_2Cl_2 (5 cm^3) and stirred at 0 °C for 1 h. Diethyl ether (20 cm^3) was added and the mixture was left at −20 °C for 12 h. The microcrystalline orange solid was collected by filtration and vacuum dried (0.046 g, 73%), m.p. 143 °C (decomp.). *Anal.* Found: C, 54.42; H, 3.52; N, 5.43. Calc. for $C_{44}H_{38}F_6N_4P_3Rh \cdot 0.5CH_2Cl_2$: C, 54.81; H, 4.03; N, 5.74%. Molar conductivity: Λ_M 77.80 $\Omega^{-1}\ mol^{-1}\ cm^2$ (10^{-3} mol dm^{-3}) in nitromethane. IR (KBr disc): ν(Rh–H) 2070 br cm^{-1}. NMR data: δ_H (300 MHz, $(CD_3)_2CO$, standard Me_4Si) 8.95 (1H, brd, $J = 6.0$ Hz, not assigned), 8.84 (2H, dd, $J = 6.0$, $J = 1.5$ Hz, not assigned).

Crystal Structure Determination

A yellow prismatic crystal of approximate dimensions 0.32 × 0.34 × 0.48 mm was used for the X-ray analysis. Unit-cell parameters were obtained by least-squares refinement of the θ values of 30 reflections carefully measured in the θ range 10–15°.

Crystal data

$C_{50}H_{42}F_6N_4P_3Rh \cdot CH_2Cl_2$, $M = 1093.66$, monoclinic, $a = 18.629(6)$, $b = 15.339(5)$, $c = 17.146(5)$ Å, $\beta = 101.02(3)°$, $U = 4809(3)$ Å^3, space group $P2_1/a$, $Z = 4$, $D_c = 1.511$ g cm^{-3}, $F(000) = 2224$, μ(Mo Kα) = 6.21 cm^{-1}.

Data Collection and Processing

Data were collected at room temperature on a Siemens AED diffractometer using the niobium-filtered Mo Kα radiation ($\lambda = 0.71069$ Å) and the $\theta/2\theta$ scan mode, the individual reflections profiles having been analyzed according to Lehmann and Larsen [31]. 11274 reflections in the range $3 \leqslant \theta \leqslant 27°$ were measured and 6225, having $I \geqslant 2\sigma(I)$, were considered observed and used in the analysis. No correction for the absorption was applied because of the low value of μR.

Structure Solution and Refinement

The structure was solved by Patterson and Fourier methods and the refinement was carried out by means of the SHELX system of computer programs [32]; first by full-matrix least-squares with isotropic thermal parameters, then by block-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms excepting those of the anion and solvent molecule. All the hydrogen atoms were clearly localized in the final ΔF map, but unfortunately their refinement was unsuccessful.

The weighting scheme used in the last cycles of refinement was $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ with $K = 0.5285$ and $g = 0.019$. Final R and R' values were 0.076 and 0.093 respectively. Final atomic coordinates for the non-hydrogen atoms are given in Table III. Atomic scattering factors, corrected for the anomalous dispersion of Rh, P and Cl, were taken from ref. 33. All calculations were performed on the CRAY X-MP/12 computer of the 'Consorzio per la gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale' (CINECA, Casalecchio, Bologna). In addition to the quoted program, PARST [34] and ORTEP [35] programs have been used.

Supplementary Material

Atomic coordinates for the hydrogen atoms, thermal parameters and a list of calculated and observed structure factors are available from the authors on request.

Acknowledgement

We thank the Italian Ministero della Pubblica Istruzione for financial support.

References

1 S. Ernst and W. Kaim, *J. Am. Chem. Soc., 108*, 3578 (1986).

2 Q. Jaradat, K. Barquawi and T. S. Akashed, *Inorg. Chim. Acta, 116*, 63 (1986), and refs. therein.

3 A. Tiripicchio, A. M. Manotti Lanfredi, M. Ghedini and F. Neve, *J. Chem. Soc., Chem. Commun.*, 97 (1983).

4 M. Ghedini and F. Neve, *J. Chem. Soc., Dalton Trans.*, 1417 (1984).

5 M. Ghedini, F. Neve, F. Morazzoni and C. Oliva, *Polyhedron, 4*, 497 (1985).

6 M. Ghedini, M. Longeri and F. Neve, *J. Chem. Soc., Dalton Trans.*, 2669 (1986).

7 N. Kitamura, Y. Kawanishi and S. Tazuke, *Chem. Phys. Lett., 97*, 103 (1983).

8 S. Ernst and W. Kaim, *Angew. Chem., Int. Ed. Engl., 24*, 430 (1985).

9 V. Barone, F. Lely, C. Cauletti, M. N. Piancastelli, M. Ghedini and N. Russo, *Cong. Naz. Chim. Inorg.*, [*Atti*], 533 (1986).

10 C. Cocevar, G. Mestroni and A. Camus, *J. Organomet. Chem., 35*, 389 (1972).

11 I. I. Bhayat and W. R. McWhinnie, *J. Organomet. Chem., 46*, 159 (1972).

12 R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc., 98*, 2134 (1976).

13 T. Yoshida, D. L. Thorn, T. Okano, J. A. Ibers and S. Otsuka, *J. Am. Chem. Soc., 101*, 4212 (1979).

14 E. B. Meier, R. R. Burch, E. L. Muetterties and V. W. Day, *J. Am. Chem. Soc., 104*, 2661 (1982).

15 T. Yoshida, W. J. Youngs, T. Sakaeda, T. Ueda, S. Otsuka and J. A. Ibers, *J. Am. Chem. Soc., 105*, 6273 (1983).

16 A. L. Balch, J. C. Linehan and M. M. Olmstead, *Inorg. Chem., 24*, 3976 (1985).

17 M. Di Vaira, M. Peruzzini, F. Zanobini and P. Stoppioni, *Inorg. Chim. Acta, 69*, 37 (1983).

18 A. M. Manotti Lanfredi, A. Tiripicchio, M. Ghedini and G. De Munno, *Acta Crystallogr., Sect. B, 38*, 1165 (1982).

19 A. M. Manotti Lanfredi, A. Tiripicchio, F. Ugozzoli, M. Ghedini and F. Neve, *J. Chem. Soc., Dalton Trans.*, in press.

20 M. Ghedini, G. De Munno, G. Denti, A. M. Manotti Lanfredi and A. Tiripicchio, *Inorg. Chim. Acta, 57*, 87 (1982).

21 B. A. Kelly, A. J. Welch and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 2237 (1977).

22 B. A. Coyle and J. A. Ibers, *Inorg. Chem., 11*, 1105 (1972).

23 R. G. Teller and R. Bau, *Struct. Bonding (Berlin), 44*, 1 (1981).

24 T. Yoshida, S. Otsuka, M. Matsumoto and K. Nakatsu, *Inorg. Chim. Acta, 29*, L275 (1978).

25 B. Olgemöller and W. Beck, *Inorg. Chem., 22*, 997 (1983).

26 W. Butte and F. H. Case, *J. Org. Chem., 26*, 4690 (1961).

27 J. J. Lafferty and F. H. Case, *J. Org. Chem.*, *32*, 1591 (1967).
28 R. J. Crutchley and A. B. P. Lever, *Inorg. Chem.*, *21*, 2276 (1982).
29 G. Giordano and R. H. Crabtree, *Inorg. Synth.*, *19*, 218 (1979).
30 O. W. Howarth, C. H. McAteer, P. Moore, G. E. Morris and N. W. Alcock, *J. Chem. Soc., Dalton Trans.*, 541 (1982).
31 M. S. Lehmann and F. K. Larsen, *Acta Crystallogr., Sect. A*, *30*, 580 (1974).
32 G. M. Sheldrick, 'Program for Crystal Structure Determination', University of Cambridge, 1979.
33 'International Tables for X-Ray Crystallography', Vol. 4, Kynoch Press, Birmingham, 1974.
34 M. Nardelli, *Comput. Chem.*, *7*, 95 (1983).
35 C. K. Johnson, 'ORTEP', *Report ORNI-3794 (revised)*, Oak Ridge National Laboratory, Tenn., 1965.