



Rhodium(I) complexes of the dppn ligand, 3,6-bis(2'-pyridyl)pyridazine and X-ray structure of $[\text{Rh}(\text{CO})(\text{dppn})(\text{PPh}_3)](\text{PF}_6)$

Nouredine Rahmouni,^{a,c} Ali A. Bahsoun,^a Marie-Thérèse Youinou,^a
John A. Osborn,^{a*} Jean Fischer^b and Aziz Ezzamarty^c

^a Laboratoire de Chimie des Métaux de Transition et de Catalyse

^b Laboratoire de Cristallochimie et Chimie Structurale, URA 424 C.N.R.S., Institut Le Bel,
Université Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France

^c Laboratoire de Catalyse, Université Hassan II, Faculté des Sciences Ain Chok, B.P. 5366, Maârif,
Casablanca, Maroc

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Abstract—The reaction of the 3,6-bis(2'-pyridyl)pyridazine(dppn) ligand, with one and two equivalents of $[\text{Rh}(\text{CO})_2\text{S}_n](\text{PF}_6)$, ($s = \text{THF}$), yields respectively the mononuclear complex $[\text{Rh}(\text{CO})_2(\text{dppn})](\text{PF}_6)$ **1** and the binuclear complex $[\text{Rh}_2(\text{CO})_4(\text{dppn})](\text{PF}_6)_2$ **3**. Furthermore, the reaction of **1** with PPh_3 results in a substitution reaction to give $[\text{Rh}(\text{CO})(\text{dppn})(\text{PPh}_3)_2](\text{PF}_6)$ **2**. The unsaturated complex **3** reacts with the monodentate phosphine PPh_3 to yield a mixture of the known compound $[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2](\text{PF}_6)$ and of the mononuclear $[\text{Rh}(\text{CO})(\text{dppn})(\text{PPh}_3)](\text{PF}_6)$ **4**, the crystal structure of which was established by X-ray diffraction. Moreover, **3** reacts with the bis(diphenylphosphino)methane(dppm) ligand in a 1 : 2 ratio to form the binuclear A-frame complex $[\text{Rh}_2(\text{CO})_2(\text{dppn})(\mu\text{-dppm})_2](\text{PF}_6)_2$ **5**. However, the reaction of **3** with excess dppm (1 : 4 ratio) gives the known complex $[\text{Rh}(\text{CO})(\text{dppm})_2](\text{PF}_6)$ **6**. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: 3,6-bis(2'-pyridyl)pyridazine; bis(diphenylphosphino)methane; triphenylphosphine; carbonyl; rhodium; X-ray structure.

The heterocyclic 3,6-bis(2'-pyridyl)pyridazine ligand, hereafter dppn, is interesting in that it provides two adjacent chelating sites which are able to coordinate transition metals at an internuclear distance of approximately 3.5 Å. This can allow the two metals to interact via ligand bridges or electronically across the dppn planar framework. Such properties have been exploited in several ways to synthesise, for example: (i) a binuclear Ni(II) complex [1] in which the magnetic properties denote the presence of an exchange interaction between the two metal centres; (ii) several binuclear Cu(II) complexes [2] such as $[\text{Cu}_2(\mu\text{-OH})\text{Cl}_3(\text{H}_2\text{O})(\text{dppn})]$, for which structural studies show that the hydroxy ligand bridges the two metal centres with a Cu(II) to Cu(II) separation of 3.376 Å. In $[\text{Cu}_2(\mu\text{-OH})\text{Br}_3(\text{dppn})]_n$, a polymeric stacking of

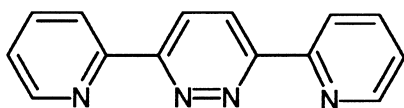
binuclear units joined through bromide ligands is found; (iii) certain heterobinuclear complexes using two separate steps with a sequential addition of one equivalent of each of metal complexes [3]; (iv) a tetranuclear Cu(I) grid-like complex, $[\text{Cu}_4(\text{dppn})_4]^{4+}$. It was seen that when one tetrahedral metal ion is incorporated into the dppn ligand, self-assembly of the monometallic units is possible to yield a complex in which the four copper atoms are coplanar and spanned by four dppn ligands. The X-ray structure determination shows that pairs of the quasi-planar dppn ligands align in parallel above and below the rhombic array of Cu_4 [4]. This principle has subsequently been expanded to the synthesis of a variety of fascinating self-assembled structures [5].

The presence of two metals held in close proximity is conceptually of great interest in homogeneous catalysts for several reasons. For example, a substrate may be activated by a simultaneous interaction with both

* Author to whom correspondence should be addressed.

metal centres. Alternatively, the two metals could serve to activate selectively different substrates, but their proximity would allow further interactions between the activated molecules. Heterobimetallic systems may be of particular interest for this type of reactivity.

In this paper we present the synthesis and characterisation of mononuclear and binuclear cationic Rh(I) complexes of the dppn ligand. Further reactions of the dirhodium complex of dppn with PPh_3 and $\text{CH}_2(\text{PPh}_2)_2$ were also studied. The single crystal X-ray structure of a monomeric dppn derivative of Rh(I) is also described.



dppn

EXPERIMENTAL

General

All reactions were carried out under an atmosphere of prepurified nitrogen or argon using standard Schlenk techniques or performed in a Vacuum Atmospheres Corporation glove box. Solvents such as Et_2O , THF and hydrocarbons were distilled from sodium and benzophenone and CH_2Cl_2 from CaH_2 under nitrogen. The 3,6-bis(2'-pyridyl)pyridazine(dppn) [6] and bis(diphenylphosphino)methane(dppm) ligands [7] as well as $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ [8] were prepared according to literature procedures. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, AgPF_6 and PPh_3 were respectively purchased from Johnson Matthey and Strem Chemicals and used as supplied.

IR spectra were recorded on a Perkin-Elmer 597 instrument. NMR spectra were run on a Bruker SY 200 spectrometer. Solvent peaks (^1H , ^{13}C NMR) served as internal references with the data fitted relatively to TMS. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were referenced to external 85% H_3PO_4 with downfield chemical shifts reported as positive. Attempts to record the mass spectra of these compounds by spectroscopic methods were unsuccessful.

Preparation of $[\text{Rh}(\text{CO})_2(\text{dppn})](\text{PF}_6)$ **1**

A solution of $[\text{Rh}(\text{CO})_2\text{S}_n](\text{PF}_6)$ ($\text{S} = \text{THF}$) prepared from a 2:1 reaction mixture of AgPF_6 (0.215 mg, 0.850 mmol) and $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (0.165 mg, 0.425 mmol) in THF (10 cm^3) was added dropwise to a solution of dppn (0.200 g, 0.850 mmol) in benzene (10 cm^3). The yellow-green precipitate which formed rapidly was separated and washed successively with

THF (2 cm^3) and CH_2Cl_2 (2 cm^3) (Yield: 85%). IR (Nujol mull, cm^{-1}) ν_{CO} 2100 (s), 2050 (s); $\nu_{\text{P-F}}$ 840 (br, s), 560 (s); $\nu_{(\text{C}=\text{C} \text{ or } \text{C}=\text{N})}$ 1600 (mw), 1590 (w). Anal: Calcd for $\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_2\text{F}_6\text{PRh}$: C, 35.71; H, 1.87; N, 10.44; Rh, 19.12. Found: C, 36.54; H, 1.52; N, 9.58; Rh, 18.13.

Preparation of $[\text{Rh}(\text{CO})(\text{dppn})(\text{PPh}_3)_2](\text{PF}_6)$ **2**

Complex **1** (0.100 g, 0.185 mmol) in acetone (5 cm^3) was added to an acetone solution (5 cm^3) of PPh_3 (0.097 g, 0.370 mmol). The light brown precipitate was filtered, washed several times with Et_2O ($3 \times 5\text{ cm}^3$) and dried under vacuum (Yield: 85%). IR (Nujol mull, cm^{-1}) ν_{CO} 1940. $^{31}\text{P}\{^1\text{H}\}$ NMR, $(\text{CD}_3)_2\text{CO}$, δ_{ppm} , 41 (d, $I = 2$, $^1J_{\text{Rh-P}} = 113\text{ Hz}$, PPh_3), -143 (hept, $I = 1$, PF_6^-). Anal: Calcd for $\text{C}_{51}\text{H}_{40}\text{N}_4\text{O}_2\text{F}_6\text{P}_3\text{Rh}$: C, 59.20; H, 3.90; N, 5.41. Found: C, 58.15; H, 3.93; N, 5.41.

Preparation of $[\text{Rh}_2(\text{CO})_4(\text{dppn})](\text{PF}_6)_2$ **3**

A solution of dppn (0.100 g, 0.425 mmol) in benzene (5 cm^3) was added to a yellow solution of $[\text{Rh}(\text{CO})_2\text{S}_n](\text{PF}_6)$ (0.850 mmol) in THF (5 cm^3). The compound **3** precipitated out as an orange microcrystalline compound which was filtered and washed with THF (2 cm^3) and then CH_2Cl_2 (2 cm^3) (Yield: 90%). IR (Nujol mull, cm^{-1}) ν_{CO} 2100 (s), 2050 (s); $\nu_{\text{P-F}}$ 840 (br, s), 560 (s); $\nu_{(\text{C}=\text{C} \text{ or } \text{C}=\text{N})}$ 1600 (mw). ^1H NMR $(\text{CD}_3)_2\text{CO}$, δ_{ppm} H arom: 9.35 (s, 2H), 9.22 (d, 2H), 8.89 (d, 2H), 8.67 (t, 2H), 8.16 (t, 2H). Anal: Calcd for $\text{C}_{18}\text{H}_{10}\text{N}_4\text{O}_4\text{F}_{12}\text{P}_2\text{Rh}_2$: C, 25.68; H, 1.20; N, 6.65; P, 7.36; Rh, 24.44. Found: C, 26.35; H, 1.28; N, 6.25; P, 7.25; Rh, 23.26.

Preparation of $[\text{Rh}(\text{CO})(\text{dppn})(\text{PPh}_3)](\text{PF}_6)$ **4**

A solution of PPh_3 (0.093 g, 0.356 mmol) in CH_2Cl_2 (5 cm^3) was added dropwise to a slurry of the dimer **3** (0.100 g, 0.119 mmol) in CH_2Cl_2 (5 cm^3) under vigorous stirring for 1 h. The deep red solution was filtered over celite and evaporated to dryness. After recrystallisation from CH_2Cl_2 /hexane, a mixture of yellow crystals of the known complex $[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2](\text{PF}_6)$ [9] and of red crystals of $[\text{Rh}(\text{CO})(\text{dppn})(\text{PPh}_3)](\text{PF}_6)$ **4** was obtained. For **4**: IR (Nujol mull, cm^{-1}) ν_{CO} 2000 (s); $^{31}\text{P}\{^1\text{H}\}$ NMR $(\text{CD}_3)_2\text{CO}/\text{CH}_2\text{Cl}_2$, δ_{ppm} , 42.24 (d, $I = 1$, $J_{\text{Rh-P}} = 150\text{ Hz}$, PPh_3), -142 (hept, $I = 1$, PF_6^-). X-ray quality crystals of **4** $\cdot (\text{CH}_3)_2\text{CO}$ were obtained from a 1:1 mixture of acetone/ethanol.

Preparation of $[\text{Rh}_2(\text{CO})_2(\text{dppn})(\mu\text{-dppm})_2](\text{PF}_6)_2$ **5**

To a suspension of **3** (0.100 g, 0.119 mmol) in CH_2Cl_2 (5 cm^3) was added dropwise a solution of dppm (0.091 g, 0.237 mmol) in CH_2Cl_2 (5 cm^3). The

reaction mixture was allowed to stir for 2 h during which a deep green colour developed. The green precipitate which formed after addition of Et₂O (40 cm³) was filtered off, washed successively with C₆H₆ and Et₂O and dried under vacuum (Yield: 90%). IR (Nujol mull, cm⁻¹), besides specific absorptions due to dppn and PF₆⁻, ν_{CO} 2000 (vs). ³¹P{¹H} NMR (CD₂Cl₂, δ_{ppm}), 24.5 (m, *I* = 4) and -143 (hept, *I* = 2). ¹H NMR (CD₂Cl₂, δ_{ppm}), 9.4–8 and 7.6–6.8 (m, H arom), 4.03 (m, —CH₂). Anal: Calcd for C₆₆H₅₄N₄O₂F₁₂P₆Rh₂: C, 50.99; H, 3.50; N, 3.60; P, 11.97; Rh, 13.24. Found: C, 49.50; H, 3.65; N, 3.70; P, 12.14; Rh, 12.80.

Reaction of 3 with an excess of dppn to give [Rh(CO)(dppn)₂](PF₆) 6

A solution of dppn (0.182 g, 0.473 mmol) in CH₂Cl₂ (5 cm³) was added to a slurry of the dimer **3** (0.100 g, 0.119 mmol) in CH₂Cl₂ (5 cm³). The mixture was stirred for 2 h at room temperature and the solvent evaporated to dryness under vacuum. A yellow product **6** was extracted with ether (Yield: 90%). IR (Nujol mull, cm⁻¹) ν_{CO} 1945 (s). ³¹P{¹H} NMR (CD₂Cl₂, δ_{ppm}) -19.5 (d, *I* = 4, *J*_{Rh-P} = 103 Hz, dppn), and -143 (hept, *I* = 1, PF₆⁻). ¹H NMR ((CD₃)₂CO, δ_{ppm}) 7.2–7.5 (m, H arom.), 4.5 ppm (m, —CH₂). Anal: Calcd for C₅₁H₄₄O₂F₆P₃Rh: C, 58.62; H, 4.21; P, 14.85; Rh, 9.86. Found: C, 58.24; H, 4.08; P, 14.13; Rh, 9.84.

X-ray crystal structure analysis of [Rh(CO)(dppn)(PPh₃)](PF₆)·acetone, 4·acetone

Suitable red single crystals for **4**·acetone were obtained by recrystallisation from an acetone-ethanol mixture at room temperature. One single crystal was cut out from a cluster of deep red crystals and mounted on a rotation-free goniometer head. A systematic search in reciprocal space using a Enraf-Nonius CAD4-F automatic diffractometer showed that crystals of **4**·acetone belong to the triclinic system. Quantitative data were obtained at room temperature. All experimental parameters used are given in Table 1. The resulting data set was transferred to a VAX computer, and for all subsequent calculations the Enraf-Nonius Molen package was used [10]. Three standard reflections were measured every hour during the entire data period showed no significant trend. The raw data were converted to intensities and corrected for Lorentz and polarisation factors. Absorption corrections derived from the Φ scans of 4 reflections were applied. The structure was solved using the heavy atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C—H = 0.95 Å) and isotropic temperature factors

Table 1. X-ray experimental data for **4**·acetone

Formula	C ₃₃ H ₂₅ N ₄ OPRh ·PF ₆ ·OC(CH ₃) ₂
Molecular weight	830.5
Colour	red
Crystal system	triclinic
<i>a</i> (Å)	13.321(4)
<i>b</i> (Å)	13.405(4)
<i>c</i> (Å)	10.603(3)
α (°)	97.72(2)
β (°)	111.26(2)
γ (°)	84.75(2)
<i>V</i> (Å ³)	1746.6
<i>Z</i>	2
<i>D</i> _{calc} (g cm ⁻³)	1.579
Wavelength (Å)	0.7107
μ (cm ⁻¹)	6.396
Space group	<i>P</i> -1
Diffractometer	Nonius CAD4-F
Crystal size (mm)	0.23 × 0.28 × 0.35
<i>T</i> (K)	293
Radiation	Mo- <i>K</i> _α graphite mono-chromated
Mode	θ/θ
Scan speed	variable
Scan width (°)	1.00 + 0.34 × tg(θ)
Octants	± <i>h</i> ± <i>k</i> + 1
θ min/max (°)	2/23
Number of data collected	4885
Number of data with <i>I</i> > 3 σ (<i>I</i>)	3166
Number of variables	460
Abs min/max	0.73/1.09
<i>R</i> (<i>F</i>)	0.043
<i>Rw</i> (<i>F</i>)	0.056
<i>P</i>	0.08
Largest peak in final diff. (e Å ⁻³)	0.10
GOF	1.095

such as B(H) = 1.3 Beqv(C) Å² but not refined. Full least squares refinements: $\sigma^2(F^2) = \sigma^2 \text{ counts} + (pI)^2$. A final difference map revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come respectively from [11]. Table 1 lists experimental details and final results.

RESULTS AND DISCUSSION

The deep yellow-green compound, [Rh(CO)₂(dppn)](PF₆) **1**, was obtained in high yield by the reaction of equimolar amounts of [Rh(CO)₂(THF)₂](PF₆) and dppn [6]. The IR spectrum of **1** displays two strong absorptions at 2100 and 2050 cm⁻¹, typical of terminal *cis* carbonyl ligands and similar to those reported for the analogous 2,2'-bipyridine of *o*-phenanthroline carbonyl complexes of Rh(I)[12,13]. Hence one chelating site of the dppn ligand is coordinated to the Rh(I) centre completing the square planar configuration for **1**. The reaction of **1** with PPh₃ (1 : 2 mol ratio) gives a brick red complex

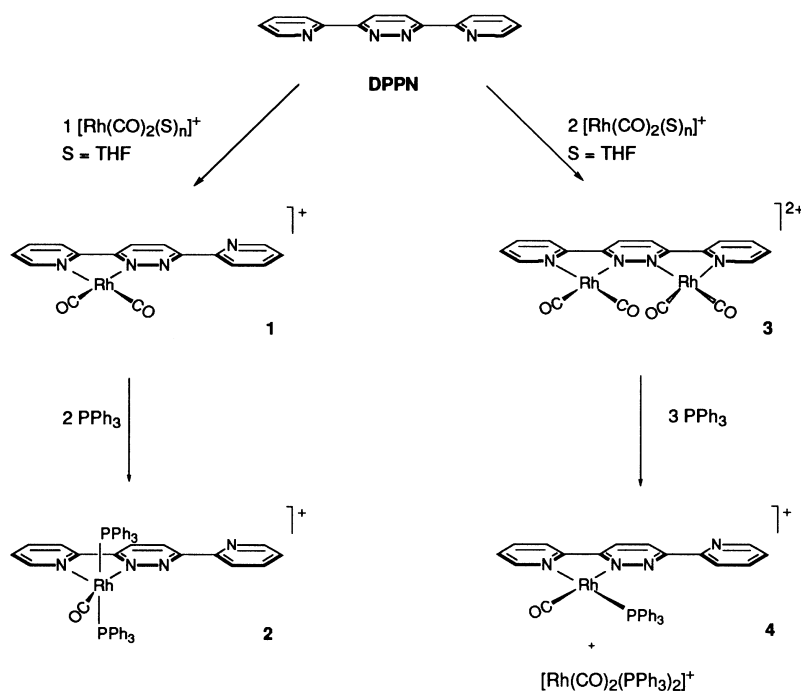
which analyses as $[\text{Rh}(\text{CO})(\text{dppn})(\text{PPh}_3)_2](\text{PF}_6)_2$ **2**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a doublet at 41 ppm [$J(\text{Rh}-\text{P}) = 113 \text{ Hz}$] which suggests a trigonal bipyramid configuration for the pentacoordinated Rh(I) derivative [13] with two axial PPh_3 ligands and an equatorial CO ligand which is also revealed by the presence of a strong absorption band at 1940 cm^{-1} in the IR spectrum.

When two equivalents of $[\text{Rh}(\text{CO})_2(\text{THF})_n](\text{PF}_6)_2$ are added to one equivalent of dppn in a THF/ C_6H_6 mixture, an orange dimeric complex **3**, corresponding to $[\text{Rh}_2(\text{CO})_4(\text{dppn})](\text{PF}_6)_2$, is obtained. Its ^1H NMR spectrum shows five aromatic resonances of equal intensity as one singlet, two doublets and two triplets indicating that both coordination sites of the dppn ligand are occupied by Rh(I) ions. Also, the IR spectrum in the carbonyl region shows only two terminal ν_{CO} absorptions at 2100 and 2050 cm^{-1} . Hence we can propose the symmetric binuclear structure shown in Scheme 1.

However, one Rh(I) in **3** can be relatively easily removed by ligands such as phosphines (Scheme 1). Treatment of **3** with PPh_3 gives $[\text{Rh}(\text{CO})_2(\text{PPh}_3)_2](\text{PF}_6)_2$ [9] and $[\text{Rh}(\text{CO})(\text{dppn})(\text{PPh}_3)](\text{PF}_6)_2$ **4**, the formation of which can be followed by ^{31}P NMR. We have structurally characterised **4** ($\text{CH}_3)_2\text{CO}$ by X-ray diffraction (Fig. 1), which enables us in part to understand the instability of the binuclear unit. The distorted square planar Rh(I) cation is quasi-symmetrically coordinated to the two nitrogen atoms (N1 and N12) by one chelating site of the dppn ligand. The two

Rh—N distances (Rh—N1 = $2.090(5) \text{ \AA}$) and Rh—N12 = $2.096(5) \text{ \AA}$ and the Rh—CO of $1.833(7) \text{ \AA}$ as well as the Rh—P of $2.267(2) \text{ \AA}$ are within the range of expected bond lengths for this type of Rh(I) cation. Selected bond distances and angles are given in Table 2. The unexpected feature of this structure is the coordination of PPh_3 to Rh(I) in a *trans* position to N12 of the pyridyl arm and *cis* to the *N*-pyridazine, whereas simple steric considerations might have placed the PPh_3 *cis* to N12. The result is that the phenyl groups of the phosphine block the free chelating site of dppn which may be responsible for the loss of Rh(I) from this site. We therefore sought to stabilise the bimetallic unit in **3** by use of the bis(di-phenylphosphino)methane ligand (dppm), which is well known to form binuclear A-Frame structures (Scheme 2).

Treatment of the unsaturated dimer **3** with dppm in CH_2Cl_2 (1 : 2 molar ratio) gives a deep green compound isolated in reasonable yield, which analyses as $[\text{Rh}_2(\text{CO})_2(\text{dppn})(\text{dppm})_2](\text{PF}_6)_2$ **5**. Its IR spectrum in Nujol mull displays a very strong absorption ν_{CO} at 2000 cm^{-1} , characteristic of terminal carbonyls, as well as absorption bands due to the coordinated ligands dppn and dppm and to the PF_6^- anion. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows one signal due to coordinated dppm at $\delta = 24.5 \text{ ppm(m)}$, indicating that **5** possesses only equivalent phosphorus environments, while the ^1H NMR spectrum reveals the presence of a symmetrically coordinated dppn. Therefore the spectroscopic features indicate the formation of a classical



Scheme 1.

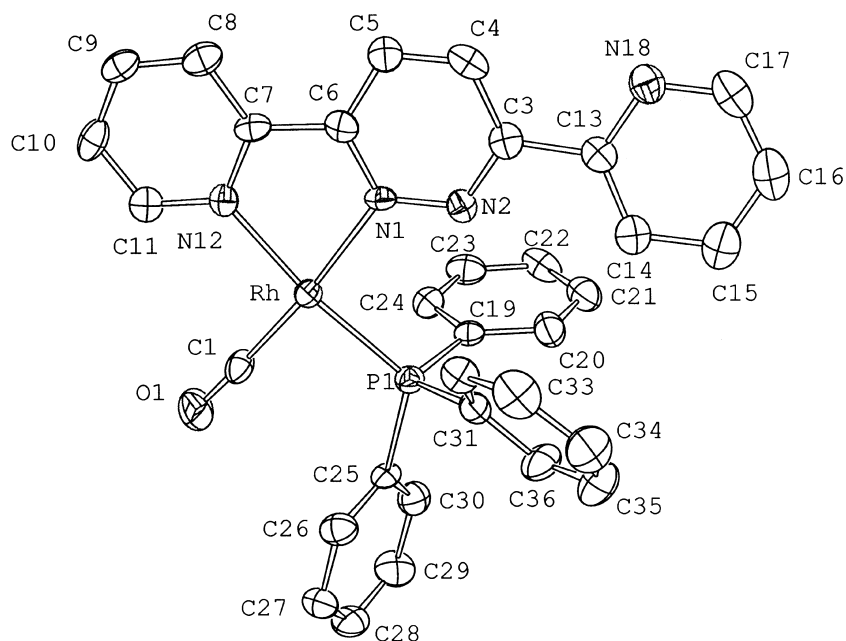


Fig. 1. Ortep plot of one molecule of **4**·acetone showing the numbering scheme used. Ellipsoids are scaled to enclose 50% of the electronic density. Hydrogen and solvate atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for [Rh(CO)(dppm)(PPh₃)](PF₆)·acetone

Rh—C1	1.833(7)	C8—C9	1.387(9)
Rh—N1	2.090(5)	C7—N12	1.353(7)
Rh—N12	2.096(5)	C9—C10	1.367(9)
Rh—P1	2.267(2)	C10—C11	1.377(9)
C1—O1	1.141(7)	C11—N12	1.341(8)
N1—N2	1.346(7)	C13—C14	1.375(9)
N1—C6	1.344(7)	C13—N18	1.338(8)
N2—C3	1.325(8)	C14—C15	1.395(9)
C3—C4	1.409(9)	C15—C16	1.36(1)
C3—C13	1.491(9)	C16—C17	1.38(1)
C4—C5	1.346(9)	C17—N18	1.330(9)
C5—C6	1.402(8)	P1—C19	1.841(7)
C6—C7	1.468(8)	P1—C25	1.823(6)
C7—C8	1.382(8)	P1—C31	1.832(6)
C1—Rh—N1	174.5(2)	N12—Rh—P1	172.7(1)
C1—Rh—N12	97.0(2)	Rh—C1—O1	177.4(6)
C1—Rh—P1	89.6(2)	N1—C6—C7	115.5(5)
N1—Rh—N12	77.5(2)	C6—C7—N12	115.1(5)
N1—Rh—P1	95.9(1)		

geometry (TBP) based on the CO ligand and a chelating site of the dppm ligand in the equatorial plane.

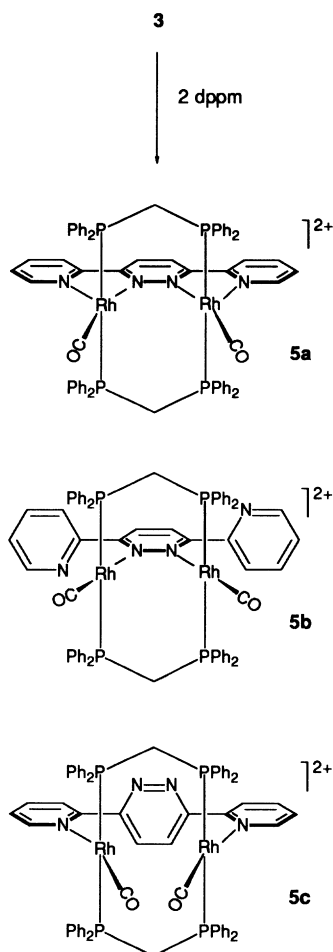
However we cannot exclude two other structural possibilities where only either the central pyridazine or the two pyridine end groups are coordinated to rhodium, as in **5b** and **5c** respectively; both Rh(I) atoms would then possess a 16e[−] configuration. Such structures gain support from preliminary studies which show that this complex reacts rapidly with CO and H₂, more typical of an unsaturated Rh(I) centre. Further studies of this compound and its reactivity are in progress.

Finally, we found that the reaction of four equivalents of dppm with complex **3** in CH₂Cl₂ occurs with the total displacement of the dppm ligand, yielding a complex **6** having an analogous formulation to that already synthesised by another route [Rh(CO)(dppm)₂]⁺ [14]. Its spectroscopic features, including the IR spectrum (ν_{CO} at 1945 cm^{−1}) and the ³¹P{¹H} NMR data in CD₂Cl₂ (δ = −19.5 ppm (d), with ¹J_{Rh-P} = 103 Hz), are closely similar to those previously reported.

CONCLUSION

A-frame type structure as in **5a** with two bridging dppm units occupying mutually *trans* positions at the two Rh(I) centres and with the tetradentate dppm ligand as third bridge. Each Rh(I) would then possess a 18e[−] configuration with a trigonal bipyramidal

The 3,6-bis(2'-pyridyl)pyridazine ligand, which possesses two contiguous binding sites for metal ions, has been found to form both mononuclear and binuclear complexes with Rh(I). However, the binuclear compounds were found to be relatively lab-



Scheme 2.

ile but their stability could be increased, in part, by the binding of further bridging ligands such as dpmm.

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REFERENCES

1. Ball, P. W. and Blake, A. B., *J. Chem. Soc. (A)*, 1969, 1415.
2. Ghedini, M., De Munno, G., Denti, G., Manotti-Lanfredi, A. M. and Tiripicchio, A., *Inorg. Chim. Acta*, 1982, **57**, 87; Dapporto, P., De Munno, G., Segà, A. and Mealli, C., *Inorg. Chim. Acta*, 1984, **83**, 171.
3. Ghedini, M., Neve, F., Morazzoni, F. and Oliva, C., *Polyhedron*, 1985, **4**, 497; Tiripicchio, A., Manotti-Lanfredi, A. M., Ghedini, M. and Neve, F., *J. Chem. Soc., Chem. Commun.*, 1983, 97.
4. Youinou, M.-T., Rahmouni, N., Fischer, J. and Osborn, J. A., *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 733.
5. Baxter, P. N. W., Lehn, J.-M., Fischer, J. and Youinou, M.-T., *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2284; Warrenner, R. N., Else, G. M., Sankar, I. V., Butler, D. N., Pekos, P. and Kennard, C. H. L., *Tetrahedron Lett.*, 1994, **35**, 6745.
6. Butte, W. A. and Case, F. H., *J. Org. Chem.*, 1961, **26**, 4690.
7. Sommer, K., *Z. Anorg. Allg. Chem.*, 1970, **376**, 37.
8. McCleverty, J. A. and Wilkinson, G., *Inorg. Synth.*, 1966, **VIII**, 211.
9. Hieber, W. and Frey, V., *Chem. Ber.*, 1966, **99**, 2614.
10. Fair, C. F. In *MolEN: An Interactive Intelligent System for Structure Analysis*, Nonius, Delf, The Netherlands, 1990.
11. Cromer, D. T. and Waber, J. T., *International Tables for X-ray Crystallography*, Vol. IV, The Kynoch Press, Birmingham, England, 1974, Table 2.2b; Table 2.3.1.
12. Reddy, G. K. N. and Susheelamma, C. H., *J. Chem. Soc., Chem. Commun.*, 1970, 54.
13. Cocevar, C., Mestroni, G. and Camus, A., *J. Organomet. Chem.*, 1972, **35**, 389.
14. Pignolet, L. H., Doughty, D. H., Nowicki, S. C. and Casalnuovo, A. L., *Inorg. Chem.*, 1980, **19**, 2172.