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# MOLECULAR STRUCTURE AND REACTIONS OF $[RhH_2(C_6H_5NCHCHNC_6H_5)(PPh_3)_2]PF_6$

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## Summary

The structure of $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]PF_6$ (Ph-DAB = 1,4-phenyl-diaza-1,3-butadiene) has been determined. The complex crystallizes in space group $P2_1/n$ of the monoclinic system, with 4 formula units in a cell of dimensions: $a$ 15.136(1), $b$ 17.842(1), $c$ 17.363(1) Å, $\beta$ 106.7(1)°. The structural data were refined by full matrix least squares methods to a conventional $R$ index of 0.073 based on those 3309 reflections having $I_0 > 3\sigma(I_0)$.

The coordination polyhedron around the rhodium may be regarded as a distorted octahedron with two hydride hydrogen atoms in *cis* position and two phosphine ligands bent towards the hydrides, making an angle $P^1RhP^2$ of 159.4(1)°. The Ph-DAB acts as a $\sigma,\sigma'$,N,N′-chelating ligand with a planar N=C–C=N skeleton in the same plane as the rhodium.

The structure is consistent with the $^1H$, $^{13}C$ and $^{31}P$ NMR data. The reactions of the title compound with CO, IMe and MeOOCC≡CCOOMe has been investigated. In all cases evolution of $H_2$ was observed.

## Introduction

The synthesis and reactions of cobalt and rhodium complexes with bidentate chelating systems (bipy or phen) (with delocalized electronic structures) was studied years ago by Cocevar et al. [1]. Complexes of general formula $RuH_2(R\text{-}DAB)(PPh_3)_2$ were obtained recently [2], in which the chelate is a 1,4-diaza-1,3-butadiene, R-DAB, with a skeleton N=C–C=N. These ligands are basic and stabilize $\sigma$-M–C bonds, but also have a strong $\pi$-back-bonding capacity and thus stabilize metals in a low oxidation state. M–H bonds are stabilized by the presence of phosphine ligands.

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In a previous paper [3] we have presented the synthesis and spectroscopic characterization of dihydride complexes of rhodium(III) of general formula $[RhH_2(R\text{-}DAB)(PR_3)_2]X$. We describe here the crystal structure of $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]PF_6$ and the reactions of this compound with CO, IMe, MeOOCC≡CCOOMe(DMC), $N_2$, and PhC≡CH.

## Results and discussion

Reaction of $[Rh(COD)(Ph\text{-}DAB)]^+$ with $PPh_3$ and molecular hydrogen gave $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]PF_6$ (I). Recrystallization from $CH_2Cl_2$/MeOH/ether, yielded prismatic shaped, red-orange crystals, which were used in the structure determination.

The previously published $^1H$ and $^{31}P$ NMR data [3] are supplemented here with $^{13}C$ NMR (Table 4). All the data are consistent with the crystal structure.

### *Molecular structure of* $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]PF_6$

The structure of the title compound is illustrated in Fig. 1, with the atoms labelled. Crystal data and processing information are given in Table 1. Final atomic coordinates and equivalent isotropic temperature factors, with estimated standard deviations, are listed in Table 2. Bond lengths and angles in the coordination sphere of the rhodium are given in Table 3 *.

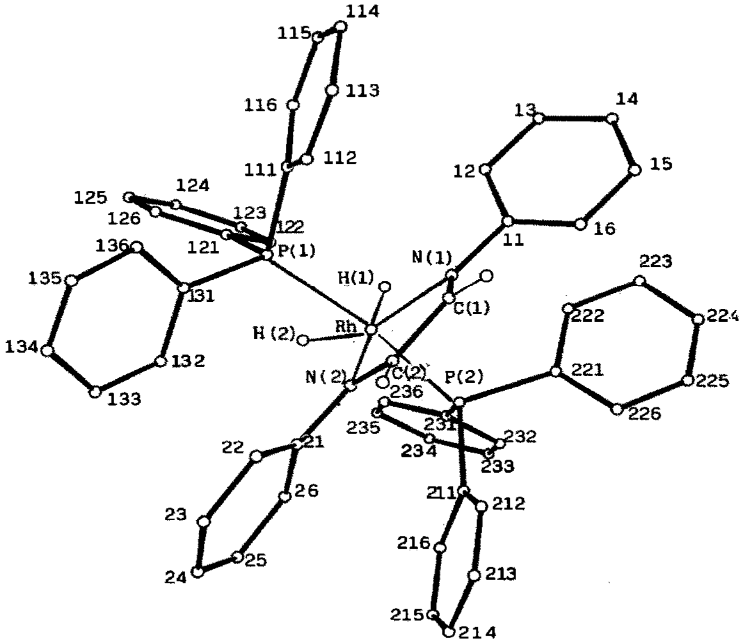

Fig. 1. View of the cationic complex $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]PF_6$ showing the atomic numbering scheme.

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* Supplementary material is available from the authors.

TABLE 1

CRYSTAL DATA AND DETAILS OF DATA COLLECTION (AT ROOM TEMPERATURE) AND STRUCTURE REFINEMENT

| | |
|---|---|
| *Crystal data* | |
| Formula | $C_{50}H_{44}N_2F_6P_3Rh$ |
| M.W. | 981.9 g.mol$^{-1}$ |
| Crystal habit | Orange transparent prismes |
| Symmetry | Monoclinic $P2_1/n$ |
| Unit cell determination | Least squares fit to 60 reflexions |
| Unit cell dimensions | $a$ 15.136(1) Å, $b$ 17.842(1) Å, $c$ 17.363(1) Å,$\beta$ 106.7(1)° |
| Packing: $V$(Å$^3$), $Z$ | 4491.9(5), 4 |
| $D$(g cm$^{-3}$) ($F$(000)) | 1.45, 2008 |
| *Experimental data* | |
| Radiation and technique | Mo-$K_\alpha$; Nonius CAD4 diffractometer |
| Monochromator | graphite |
| Scan mode (w/2$\theta$) | 1.5° scan width, 1.5 min/reflex |
| Scanning range for $\theta$ | $2 < \theta < 30$ |
| Total independent data | 9561 |
| Observed data ($I > 3\sigma(I)$) | 3309 |
| Standards for intensity control | every 90 min |
| Absorption coefficient | 5.39 cm$^{-1}$ |
| *Solution and refinement* | X-ray system [12] Computer VAX/750 |
| Solution mode | Patterson and Fourier syntheses |
| Refinement mode | Least squares on $F$'s. Observed reflexions only |
| Final shift/error | 1.88 |
| Parameter: no. of variables | 553 |
| $w$-scheme | Empirical such as to give no trends in $< W\Delta^2 >$ US $< F >$ or $< \sin\theta/\lambda$ [13] |
| $\Delta F$ final | 2.6 eÅ$^{-3}$ in the neighbourhood of the Rh atom |
| $R$; $R_w$ | 0.073; 0.060 |
| Atomic factors | Neutral atoms: International Tables for X-ray Crystallography; Anomalous dispersion applied for Rh, P and F [14]. |

The coordination polyhedron around the rhodium may be described as a distorted octahedron, with the phosphine ligands bent towards the hydride ligands. The Ph-DAB ligand is $\sigma$N-$\sigma$N′ coordinated, with the N=C–C=N skeleton essentially planar and in the same plane as the rhodium. The phenyl rings of Ph-DAB make angles of 40.4(4)° and 35.4(3)° with this plane.

Structural studies have been carried out on several R-DAB complexes but not previously on a Ph-DAB derivative [4]. Comparison of our results with those in the literature reveals a lengthening of the C=N, C–C and Rh–N bonds, (C=N, 1.276(18) Å, C–C, 1.487(20) Å; Rh–N, 2.158(11) Å). These increases may be a consequense of a smaller M → Ph-DAB $\pi$-backbonding due to the inductive effect of the phenyl ring, which gives rise to an increase in the charge density in this ligand. In addition, the length of the Rh–N bond may also be increased by the *trans* effect of the hydride ligands.

The angles of the 5-membered $\overline{N^1{=}C^1{-}C^2{=}N^2Rh}$ ring in the structure described here agree with those for other R-DAB complexes [4]; angles $N^1C^1C^2$ and $N^2C^2C^1$ are 119.(1)° and 117(1)°, respectively, and angle $N^1RhN^2$ is 77.2(4)°.

TABLE 2

ATOMIC PARAMETERS FOR $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]PF_6$

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Rh | 0.04200(7) | 0.16732(7) | −0.17606(6) | 26(0) |
| P(1) | 0.05088(24) | 0.24563(21) | −0.06742(21) | 26(1) |
| C(111) | 0.10319(75) | 0.33447(88) | −0.07687(67) | 28(4) |
| C(112) | 0.19681(86) | 0.33764(101) | −0.07356(78) | 41(5) |
| C(113) | 0.23909(104) | 0.40116(101) | −0.08998(96) | 51(7) |
| C(114) | 0.18784(110) | 0.46768(96) | −0.10765(89) | 51(7) |
| C(115) | 0.09211(106) | 0.46780(90) | −0.10854(88) | 47(6) |
| C(116) | 0.05337(107) | 0.40189(89) | −0.09283(87) | 44(6) |
| C(121) | −0.05996(86) | 0.27034(81) | −0.04888(77) | 31(5) |
| C(122) | −0.14146(102) | 0.26506(92) | −0.11065(97) | 50(7) |
| C(123) | −0.22610(95) | 0.28363(100) | −0.09511(100) | 52(7) |
| C(124) | −0.22524(108) | 0.30944(95) | −0.02194(107) | 56(7) |
| C(125) | −0.14348(113) | 0.31366(83) | 0.04162(88) | 49(7) |
| C(126) | −0.06137(105) | 0.29474(95) | 0.02571(85) | 50(7) |
| C(131) | 0.11558(95) | 0.20875(83) | 0.02959(82) | 33(6) |
| C(132) | 0.09770(95) | 0.13477(85) | 0.05018(86) | 34(5) |
| C(133) | 0.14522(121) | 0.10291(91) | 0.12203(99) | 49(7) |
| C(134) | 0.20821(126) | 0.14489(114) | 0.17652(114) | 68(9) |
| C(135) | 0.23044(125) | 0.21521(112) | 0.15812(92) | 67(8) |
| C(136) | 0.18126(108) | 0.24974(96) | 0.08642(88) | 56(7) |
| P(2) | −0.02153(23) | 0.08932(20) | −0.28435(20) | 25(1) |
| C(211) | 0.03029(87) | −0.00354(77) | −0.27368(77) | 32(5) |
| C(212) | 0.12438(96) | −0.01233(90) | −0.26496(88) | 44(6) |
| C(213) | 0.16622(117) | −0.07901(114) | −0.24545(105) | 62(8) |
| C(214) | 0.11684(127) | −0.14187(101) | −0.23602(106) | 63(8) |
| C(215) | 0.02423(119) | −0.13558(87) | −0.24343(97) | 59(7) |
| C(216) | −0.01929(96) | −0.06825(81) | −0.26456(85) | 40(6) |
| C(221) | −0.01634(90) | 0.12369(83) | −0.38226(75) | 33(5) |
| C(222) | −0.05793(89) | 0.19102(72) | −0.41018(83) | 33(5) |
| C(223) | −0.05744(102) | 0.21889(94) | −0.48465(95) | 49(6) |
| C(224) | −0.01393(110) | 0.18077(109) | −0.53096(81) | 55(7) |
| C(225) | 0.02873(110) | 0.11284(100) | −0.50410(99) | 53(7) |
| C(226) | 0.02820(105) | 0.08422(90) | −0.43079(93) | 48(6) |
| C(231) | −0.14263(86) | 0.07121(78) | −0.30348(80) | 31(5) |
| C(232) | −0.19160(96) | 0.03777(96) | −0.37682(95) | 49(6) |
| C(233) | −0.28595(88) | 0.02100(77) | −0.39179(78) | 41(6) |
| C(234) | −0.33143(93) | 0.03692(108) | −0.33617(105) | 63(7) |
| C(235) | −0.28320(100) | 0.06876(102) | −0.26425(103) | 55(7) |
| C(236) | −0.19011(96) | 0.08582(92) | −0.24860(87) | 42(6) |
| N(1) | 0.13441(67) | 0.22242(61) | −0.23227(61) | 29(4) |
| C(1) | 0.21677(86) | 0.19748(77) | −0.20722(85) | 34(5) |
| C(2) | 0.23820(90) | 0.13624(84) | −0.14658(92) | 40(6) |
| N(2) | 0.17148(67) | 0.11140(58) | −0.12279(63) | 28(4) |
| C(11) | 0.11531(86) | 0.27772(72) | −0.29326(76) | 27(5) |
| C(12) | 0.05597(100) | 0.33550(98) | −0.28905(78) | 46(6) |
| C(13) | 0.03874(130) | 0.39155(94) | −0.34921(108) | 68(8) |
| C(14) | 0.07757(143) | 0.38676(109) | −0.41032(116) | 73(9) |
| C(15) | 0.13477(120) | 0.32906(130) | −0.41421(96) | 64(8) |
| C(16) | 0.15381(98) | 0.27312(81) | −0.35407(88) | 39(6) |
| C(21) | 0.19333(79) | 0.05217(70) | −0.06589(71) | 22(5) |
| C(22) | 0.27759(89) | 0.04692(80) | −0.00861(81) | 33(5) |
| C(23) | 0.29927(103) | −0.01541(99) | 0.04328(85) | 50(7) |
| C(24) | 0.23296(103) | −0.07055(87) | 0.03718(93) | 52(6) |

TABLE 2 (continued)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| C(25) | 0.14915(97) | −0.06400(83) | −0.01798(86) | 41(6) |
| C(26) | 0.12993(91) | −0.00330(87) | −0.06878(87) | 43(6) |
| P(3) | 0.02263(26) | 0.62846(23) | −0.30002(24) | 38(1) |
| F(1) | 0.07065(57) | 0.69998(50) | −0.32268(67) | 77(5) |
| F(2) | 0.00818(74) | 0.66830(78) | −0.22486(64) | 106(5) |
| F(3) | 0.03779(69) | 0.58848(66) | −0.37631(59) | 88(5) |
| F(4) | −0.02588(61) | 0.55470(49) | −0.27944(63) | 71(4) |
| F(5) | 0.12049(55) | 0.59983(60) | −0.24870(59) | 76(4) |
| F(6) | −0.07396(53) | 0.65742(64) | −0.35170(59) | 77(4) |

The Rh–P bond lengths, 2.320(4) and 2.315(3) Å in the present complex are normal for rhodium(III) complexes [5], and are very similar to those observed in $RhH_2(O_2COH)[(P(i\text{-}Pr)_3]_2$, 2.321(2) and 2.302(2) Å and only slightly shorter than several others which fall in the range 2.348–2.363 Å [6,7]. The $P^1RhP^2$ angle, in the present complex is 164.87(9)°.

### *Reactivity of* $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]PF_6$ *(I)*

The physical properties of the products from the reaction of I with CO, MeI and $MeO_2CC{\equiv}CCO_2Me$ (DMC) are given in Table 5.

*Reaction with CO.* Complex I reacts incompletely with CO at room temperature to give a yellow green monocarbonyl, which shows a strong band in its IR spectrum at 1955 $cm^{-1}$, with a shoulder at 1975 $cm^{-1}$. The $^{13}C$ NMR spectrum shows a resonance at 181 ppm corresponding to a terminal CO group. The reaction involves reductive elimination of hydrogen followed by addition of CO.

*(Continued on p. 370)*

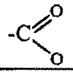
TABLE 3

IMPORTANT BOND DISTANCES (Å) AND BOND ANGLES (°) (Numbers in parentheses are e.s.d's of the last-significant digits.)

| | | | |
|---|---|---|---|
| Rh–H(1) | 1.375 | Rh–H(2) | 1.327 |
| Rh–P(1) | 2.320(4) | Rh–P(2) | 2.315(3) |
| Rh–N(1) | 2.158(12) | Rh–N(2) | 2.157(10) |
| N(1)–C(1) | 1.277(16) | C(1)–C(2) | 1.487(20) |
| N(2)–C(2) | 1.275(19) | P(1)–C(111) | 1.800(15) |
| P(1)–C(121) | 1.850(14) | P(1)–C(131) | 1.812(13) |
| P(2)–C(211) | 1.820(14) | P(2)–C(221) | 1.830(14) |
| P(2)–C(231) | 1.800(13) | N(1)–C(11) | 1.415(17) |
| N(2)–C(21) | 1.419(16) | | |
| H(1)–Rh–H(2) | 89.5(1) | N(2)–Rh–H(2) | 93.5(3) |
| N(2)–Rh–H(1) | 171.2(3) | N(1)–Rh–H(2) | 150.8(3) |
| N(1)–Rh–H(1) | 96.3(3) | P(2)–Rh–H(2) | 114.5(1) |
| P(2)–Rh–H(1) | 95.6(1) | P(2)–Rh–N(2) | 100.7(3) |
| P(2)–Rh–N(1) | 94.5(3) | P(1)–Rh–H(2) | 51.3(1) |
| P(1)–Rh–H(1) | 79.9(1) | P(1)–Rh–N(2) | 95.5(3) |
| P(1)–Rh–N(1) | 101.5(3) | P(1)–Rh–P(2) | 159.4(1) |
| N(1)–Rh–N(2) | 77.2(4) | Rh–N(1)–C(11) | 129.5(9) |
| Rh–N(1)–C(1) | 112.5(9) | N(1)–C(1)–C(2) | 119.4(12) |
| C(1)–C(2)–N(2) | 116.9(13) | Rh–N(2)–C(2) | 114.0(9) |

TABLE 4

NMR DATA ($^1H$ and $^{13}C$) FOR $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]^+$ AND PRODUCTS OF ITS REACTIONS

| Compound | $^1H$ NMR | | | | | | | | $^{13}C$ NMR | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | hydride | | Imino group | $\Delta$ [a] | Ph-DAB | $\Delta$ [a] | IMe/ Me,DMC | $\Delta$ [a] | C≡O/  | C=N | Ph | Ph-X | C≡C |
| | $\delta$ (ppm) | $J$ (Hz) | $\delta$ (ppm) | $\delta$ (ppm) | | $\delta$ (ppm) | | | | | | | |
| $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]^+$ | 15.4 (q) | 14 | 8.50 (s) | 3.66 | 7.13 (t) *p* | 0.51 | | | | 160.7 | 147.0 | 132.2 (t) | |
| | | | | | 6.91 (t) *m* | −0.19 | | | | | | 133.4 (s) | |
| | | | | | 6.72 (d) *o* | −0.06 | | | | | | 135.0 (t) | |
| $[Rh(CO)(Ph\text{-}DAB)(PPh_3)_2]^+$ | | | 8.50 (s) | 3.66 | 7.13 (t) *p* | 0.51 | | | 181.7/ | 160.1 | 146.0 | 131.8 (t) | |
| | | | | | 6.92 (t) *m* | −0.20 | | | | | | 132.9 (s) | |
| | | | | | 6.71 (d) *o* | −0.05 | | | | | | 134.3 (t) | |
| $[Rh(IMe)I(Ph\text{-}DAB)(PPh_3)_2]^+$ | | | 8.48 (s) | 3.64 | 7.28 (t) *p* | 0.66 | 1.35 br | −0.82 | | 160.6 | 148.6 | 133.5 (m) | |
| | | | | | 7.00 (t) *m* | −0.11 | | | | | | | |
| | | | | | 6.80 (d) *o* | 0.02 | | | | | | | |
| $[Rh(DMC)(Ph\text{-}DAB)(PPh_3)_2]^+$ | | | 8.49 (s) | 3.65 | 7.12 (t) | 0.50 | /3.90 | 0.05 | /170 | 160.8 | 148.6 | 133.3 | 70 |
| | | | | | 6.91 (t) | −0.19 | /3.86 | 0.01 | | | | | |
| | | | | | 6.70 (d) | −0.04 | | | | | | | |

[a] $\Delta = \delta(\text{complex}) - \delta(\text{ligand})$.

TABLE 5

PHYSICAL PROPERTIES OF $[RhH_2(Ph\text{-}DAB)(PPh_3)_n]^+$, $n = 2,1$ AND THE PRODUCTS OF ITS REACTIONS

| Compound | Colour | $\Lambda^a$ (ohm$^{-1}$ cm$^2$ mol$^{-1}$) | IR | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | $\nu(CH)_{IMe}$/ $\nu(CH)_{DMC}$ | $\nu$(Rh–H) | $\nu$(C≡O)/$\nu$(C=O) | $\nu$(C=N) | $\delta(CH)_{IMe}$/ $\delta(CH)_{DMC}$ | $\delta$(Rh–H) |
| 1 $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]^+$ | light beige | 150 | | 2060 sh<br>2040 m | | 1590 m | | 760 s |
| 2 $[Rh(CO)(Ph\text{-}DAB)(PPh_3)_2]^+$ | yellow green | 143 | | | 1975 sh/<br>1955 s / | 1600 m | | |
| 3 $[Rh(IMe)I(Ph\text{-}DAB)(PPh_3)_2]^+$ | brown | 117 | 2980 w/ | | | 1600 m | 1250 m/ | |
| 4 $[Rh(DMC)(Ph\text{-}DAB)(PPh_3)_2]^+$ | yellow | 67 | /2960 m | | /1723 s | 1580 m | /1260 m | |
| 5 $[RhH_2(Ph\text{-}DAB)(PPh_3)]^+$ | brown | 199 | | 2030 sh<br>2010 m | | 1580 w | | 760 sh<br>750 s |
| 6 $[Rh(IMe)I(Ph\text{-}DAB)(PPh_3)]^+$ | brown | 120 | | | | 1600 m | | |
| 7 $[Rh(DMC)(Ph\text{-}DAB)(PPh_3)]^+$ | yellow green | 103 | 2960 w/ | | /1730 s | 1600 m | /1270 m | |

[a] The conductivity measurements have been carried out on acetone solutions ($10^{-3}$ $M$ at 20°C).

*Reaction with MeI.* This reaction gave a brown compound that shows a resonance at 1.35 ppm (br) in its $^1$H NMR spectrum which is clearly not due to a methyl group bound directly to rhodium ($\delta$ 2.88 ppm) [8,9] and we postulate it as having a coordination of $ICH_3$ through the iodine atom. A stretching band $\nu$(C–H) and deformation band $\delta$(C–H) appear at 2980 and 1250 cm$^{-1}$, respectively, in the IR spectrum.

$H_2$ elimination occurred as in the previous reaction.

*Reaction with MeOOCC≡CCOOMe (DMC).* *Cis*-dihydrides of transition metals have received much attention as catalysts for the hydrogenation of unsaturated organic molecules [10]. In our present work, the reaction with DMC was not one of insertion, as no $^1$H NMR signal of the vinyl hydrogen was observed, so we suggested that there was a $\pi$-bond between DMC and the metal centre, this was confirmed by a resonance at 70 ppm in the $^{13}$C NMR spectra. The C=O group gives a chemical shift at 170 ppm, and a strong IR band at 1723 cm$^{-1}$.

In its $^1$H NMR spectrum, the methyl group of DMC gives two signals of different intensities at 3.90 and 3.86 ppm (relative area 6 protons). The IR spectrum shows a signal of medium intensity at 2960 cm$^{-1}$, corresponding to the C–H stretching vibration, and another at 1260 cm$^{-1}$ due to $\delta$(C–H).

The elimination of hydrogen was observed during the course of the reaction.

*Reaction with $N_2$.* Although various reaction conditions were scanned it was not possible to get a $N_2$ compound; an unidentified mixture was obtained.

*Reaction with PhC=CH.* No reaction occurred and the starting material was recovered unchanged.

### *Reactivity of $[RhH_2(Ph\text{-}DAB)(PPh_3)]X$ (II)*

The reactivity of II, the dihydride pentacoordinate complex containing only one $PPh_3$ ligand [3], was also studied in order to compare the results with those for complex I. Compounds V, VI and VII (Table 5) were obtained from the reactions with CO, MeI and DMC, respectively. Characterization of these compounds by NMR was not possible because of their poor solubility, but the analytical and spectroscopic data are consistent with the stoichiometries shown in Table 5.

## Experimental

### *1. Synthesis of $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]X$ ($X = PF_6^-$, $ClO_4^-$) (I)*

A solution of $PPh_3$ (1.5 mmol) in diethyl ether was added to a methanolic solution (15 ml) of $[Rh^I(Ph\text{-}DAB)(COD)]X$ (0.5 mmol) and molecular hydrogen was bubbled through the mixture for 3 h during which the solution became yellow. Addition of an aqueous solution of $NaClO_4$ or $NH_4PF_6$ followed by partial evaporation of the solvent left a solid precipitate, yellow in colour for $ClO_4^-$ and red-orange for $PF_6^-$ anion. Yield 70–80%.

Recrystallization from $CH_2Cl_2/CH_3OH$/petroleum ether at 0 °C gave well formed prismatic orange red crystals suitable for the structure determination.

### *2. X-ray analysis of $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]PF_6$*

The crystals were coated with paraffin oil and sealed in a Lindeman glass capillary tube.

Crystal data and the processing procedure are outlined in Table 1; the rhodium atom was readily found from a Patterson map and all remaining non-hydrogen atoms were located by Fourier and difference Fourier synthesis. At this point an absorption correction was made by the method of Walker and Stuart [15], and the structure was refined by full matrix least squares methods with anisotropic thermal parameters; H atoms were found from successive difference maps. They were included in the refinement with isotropic thermal parameters of the atoms to which they were attached.

### 3. *Reactions of* $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]PF_6$

*General.* All reactions and manipulations were carried out under $N_2$ using Schlenk techniques and at room temperature unless other conditions are specified. Reagent grade commercial starting materials were used without further purification. Solvents were carefully dried, purified, and degassed before use.

The $^1H$, $^{13}C$, $^{31}P$ NMR spectra were recorded on a Bruker WM-360 Fourier Spectrometer with saturated solutions of the complexes in $CDCl_3$.

Infrared spectra were recorded with a Nicolet 60sx (FTIS) spectrometer using KBr discs. Conductivities were determined in acetone solutions with a Philips 9501/01 conductimeter. C,H, and N, analyses were performed at the Inorganic Chemistry Department of Alcalá de Henares University (Madrid).

*(i) Reaction with CO.* A yellow solution of I (0.2 g, 0.2 mmol) in methanol (10 ml) was stirred under CO (1 atm) at room temperature for 3 h. Concentration of the reaction mixture gave a green solid, which was washed several times with diethyl ether. Yield 60–70%. Analysis. Found: C, 63.0; H, 4.6; N, 2.6. $C_{51}H_{42}F_6N_2OP_3Rh$ calc.: C, 63.6; H, 4.4; N, 2.91%.

*(ii) Reaction with IMe.* To a $CH_2Cl_2$ solution (10 ml) of I (0.2 g, 0.2 mmol) was added MeI (0.3 ml, 3 mmol). The yellow solution immediately turned red and gas was evolved. The solution was evaporated and the residue was washed with diethyl ether. Recrystallization was from $CH_2Cl$/MeOH/petroleum ether. Yield 50%. Analysis. Found: C, 50.4; H, 3.9; N, 2.0. $C_{51}H_{45}F_6IN_2P_3Rh$ calc.: C, 50.9; H, 3.7; N, 2.3%.

*(iii) Reaction with* $MeO_2CC{\equiv}CCO_2Me$ *(DMC).* A solution of I (0.2 g, 0.2 mmol) in $CH_2Cl_2$ (15 ml), was treated with DMC (0.5 ml, 4 mmol) at room temperature or heating under reflux for 3 h. The solution turned red immediately in both cases and gas evolution was observed. Evaporation left a viscous oil, to which diethyl ether was added to induce crystallization. Recrystallization from petroleum ether gave orange crystals. Yield 50%. Analysis. Found: C, 62.0; H, 4.7; N, 2.8. $C_{56}H_{48}F_6N_2O_4P_3Rh$ calc.: C, 62.4; H, 4.5; N, 2.6%.

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