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Synthesis, Characterization and Structure of Cationic Hydrides of Rhodium(III). Part II*. Crystal Structure of Dihydride(1,4-biscyclohexyl-diaza-1,3-butadiene)-bis(4-fluor-tristriphenylphosphine)rhodium(III) Perchlorate

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Abstract

The reaction between $[(R\text{-}DAB)Rh(PR_3)_2]^+$ and molecular hydrogen produces cationic *cis*-dihydride complexes of Rh(III), of general formula $[RhH_2(R\text{-}DAB)(PR_3)_2]X$. They are stable in air, 1:1 conductors and have been characterized by ^1H NMR, ^{31}P NMR, IR and elemental analysis. The tertiary phosphines employed were: PPh_3, $P(p\text{-}C_6H_4F)_3$, $PMePh_2$, PEt_3, and the R-DAB ligands (RN:CR′CR′:NR)†, Ph-DAB, c-Hex-DAB, $NH_2\text{-}DAB(CH_3,CH_3)$, t-but-DAB.

The structure of $[RhH_2(c\text{-}Hex\text{-}DAB)\{P(p\text{-}C_6H_4\text{-}F)_3\}_2]ClO_4$ has been determined by an X-ray diffraction study. Crystals are orthorhombic, space group *Pbnm*. Unit cell parameters are: $a = 13.032(1)$, $b = 18.166(2)$, $c = 21.449(2)$ Å, $Z = 4$, $R = 0.081$, $R_w = 0.082$ for 2906 reflections, with $I > 3\sigma(I)$ the rhodium atom is octahedrally coordinated with the two hydride-hydrogens and c-Hex-DAB in the equatorial plane; the two phosphine ligands are in an axial position bent towards the hydrogens making an angle of 164.9(4)°.

Introduction

The coordinatively unsaturated complexes $[R\text{-}DAB\ Rh(PR_3)_2]^+$ when treated with molecular hydrogen produce Rh(III) dihydrides of general formula: $[RhH_2(R\text{-}DAB)(PR_3)_2]^+$. A preliminary account of some of these complexes has been reported by us in a previous paper [1]. In this first study we characterized these compounds by IR, ^1H NMR and ^{31}P NMR spectroscopy. Although R-DAB ligands [2] possess versatile bonding properties in these complexes they always act as bidentate, σ,σ-N,N′ 4e donors. Up to this point two distributions of ligands were possible as far as NMR results were concerned: the two phosphine ligands in *cis* position with 2-hydrogen hydrides *trans*, or vice versa. We therefore have carried out an X-ray study of their structural characterization. The determination of the structure of two of these Rh(III) dihydrides, $[RhH_2(Ph\text{-}DAB)(PPh_3)_2]PF_6$ [3] and $[RhH_2(c\text{-}Hex\text{-}DAB)\{P(pC_6H_4F)_3\}_2]ClO_4$ with different phosphine and R-DAB ligands, has allowed us to establish their general structure. Compounds of rhodium with phosphine and R-DAB ligands have not been studied before; similar compounds of ruthenium have been described by Poilblanc *et al.* [4].

We have been working with tertiary phosphines of different basicity and R-DAB ligands with variable π accepting ability to determine their influence on the M–H bond stability.

Our attention is now focussed on their reactivity with acetylenes; they have been found to be good precursors for promoting their polymerization [5].

Experimental

Solvents were carefully dried, purified and degassed before use. All manipulations were carried out using Schlenk techniques.

The R-DAB(R′R′) ligands (R = ph, c-Hex, t-but, for R′ = H and R = NH_2 for R′ = CH_3) were prepared according to published methods [6, 7] by addition of 1 equivalent of an aqueous solution of glioxal (or diacetyl in alcohol), dropping, on a cool solution of the amine (2 equiv.) or hydracine stirred and refrigerated at 0 to −5 °C:

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†Herein they will be referred to as R-DAB when they are derivatives of glioxal or as $R\text{-}DAB(CH_3,CH_3)$ when they are derived from diacetyl.

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c-Hex-DAB. Colourless flakes, melting point (m.p.) 146–147 °C, recrystallization in methanol.

t-But-DAB. Colourless crystals, m.p. 56 °C, purified by sublimation.

ph-DAB. White powder used without further purification, d.p. 105–107 °C.

NH_2-DAB(CH_3,CH_3). m.p. 156–157 °C purified by recrystallization.

Synthesis of [RhH_2(R-DAB)(PR_3)$_2$]$^+$

A solution of the tertiary phosphine (1.5 mmol) in ethyl ether was added to a solution (15 ml) of [Rh(R-DAB)(COD)]X [1] (0.5 mmol) in methanol, and molecular hydrogen was bubbled through for 3 h. The solution became yellow or brown, depending on the ligands. On addition of an aqueous solution of $NaClO_4$ or NH_4PF_6 and partial evaporation of the solvent, a solid precipitated. Recrystallization from methanol–ethyl ether. Yield 70–80%.

Recrystallization from CH_2Cl_2/CH_3OH/petroleum ether (or acetone/ethyl ether) at 0 °C, gave well formed crystals suitable for structure determination. In general syntheses were made at room temperature; depending on the ligands, special care has to be taken with respect to the general method.

To precipitate the dihydride when $PR_3 = PEt_3$, bigger anions are needed, such as PF_6^-, or BPh_4^-, with ClO_4^- the products cannot be isolated. Alkyl phosphines have the tendency to produce oils and the product has to be extracted with ethyl ether to induce crystallization.

When $PR_3 = P(p\text{-}C_6H_4F)_3$ and R-DAB = t-but-DAB or NH_2DAB (CH_3,CH_3) the product has to be obtained in hot methanol.

Techniques

Infrared spectra were obtained in a Nicolet 60 SX (FTIS) using KBr disks.

^{1}H NMR spectra (360 MHz) were recorded on a Bruker WM-360 Fourier spectrometer, using saturated solutions of the complexes in $CDCl_3$ (5 mm tubes, 18 °C). Sweep widths of 16000 Hz and 32 K data points were necessary to observed simultaneously the hydride and ligand resonances. Broadband proton decoupled.

^{31}P NMR spectra (145.79 MHz) were obtained on the same instrument using a 10 mm tunable probehead (31000 Hz sweep width, 32 K, 90° pulse angle, 2 s relaxation delay). Chemical shifts were referenced to external 85% PO_4H_3 contained in a capillary. Selective $^{31}P\{^1H\}$ decoupling experiments were done using continuous wave irradiation at a frequency and power adequate to decouple simultaneously aliphatic and aromatic ligand resonances but not the hydride signals, which appear well separated ~15 ppm up field from TMS.

Microanalyses were performed by the Department of Inorganic Chemistry, Alcalá de Henares University.

X-ray Crystallography

A single crystal of [RhH_2(c-Hex-DAB){$P(p\text{-}C_6H_4F)_3$}$_2$]ClO_4 of approximate dimensions 0.15 × 0.20 × 0.25 mm was coated with paraffin oil, and sealed in a Lindeman glass capillary tube. Once mounted in the diffractometer one proceeds to data collection. Details of crystal and experimental data are given in Table I.

The rhodium atom was readily found from a Patterson map and all remaining non-hydrogen atoms were located by Fourier and difference Fourier synthesis. Isotropic refinement was calculated by full matrix least-squares; at this point an absorption correction was made by the method of Walker and Stuart [9], and the structure refinement was followed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms. H atoms were found from a difference map; they were included in the refinement with isotropic thermal parameters of the atom to which they were attached, and maintained fixed during refinement. Last R values were $R = 0.081$, $R_w = 0.082$.

Results and Discussion

The reactions of $[RhCl(COD)]_2$ with R-DAB, in the presence of a big anion ClO_4^- or PF_6^-, yield cationic complexes of the type: [Rh(R-DAB)(COD)]$^+$, which in the presence of tertiary phosphines and molecular hydrogen give Rh(III) dihydrides of general formula [RhH_2(R-DAB)(PR_3)$_2$]$^+$.

In Table II are listed the new complexes obtained. They are grouped for each R-DAB ligand in function of the basicity of the phosphine, to make discussion easier.

Their stoichiometries are in accordance with the spectroscopic results and their elemental analyses (C, H, N). The conductance values in acetone (at 25 °C, 10^{-3} M solutions) fall in the range 94–150 (Ω^{-1} cm^2 mol^{-1}), corresponding to 1:1 electrolytes, their colours are in the range yellow to orange.

Infrared Spectra

The IR spectra of these complexes, taken in KBr disks, show the expected bands due to the R-DAB and PR_3 ligands, and the corresponding anions (ClO_4^-, PF_6^-).

A broad band at 1090 cm^{-1}, ν(Cl–O) and a medium sharp band at 620 cm^{-1} ν(O–Cl–O), in general unsplit, indicate that the perchlorate anion does not interact with the cation. PF_6^- anion gives a broad band at 830 cm^{-1} (ν(P–F)).

The ν(Rh–H) vibration presents two frequencies in the range 2140–2010, of weak to medium intensity, which implies a *cis* position for the two hydride-hydrogens. The shift of this vibration is intimately related with the electronic donor–acceptor capabil-

TABLE I. Crystal Data, Details of Data Collection (at room temperature) and Structure Refinement of $[RhH_2(c\text{-}Hex\text{-}DAB)\{P(p\text{-}C_6H_4F)_3\}_2]ClO_4$

Crystal data	
Formula	$C_{50}H_{37}N_2O_4F_6P_2ClRh$
Molecular weight	1044.5 g mol^{-1}
Crystal habit	yellow, transparent, prisms
Symmetry	orthorhombic, *Pbnm*
Unit cell determination	least-squares fit to 55 reflex
Unit cell dimensions	*a*, 13.032(1); *b*, 18.166(2); *c*, 21.449(2) Å
Packing: V (Å^3), Z	5077.8(8), 4
D_c (g cm^{-3}), F(000)	1.37, 2116
Experimental data	
Radiation and technique	Cu Kα; four circle diffractometer: PW 1100 Philips bisecting geometry
Monochromator	graphite
Scan mode ($\omega/2\theta$)	1.5° scan width 1.5 min/refl.
Scanning range for θ	$2 < \theta < 65$
Total independent data	4467
Observed data ($I > 3\sigma(I)$)	2906
Standard for intensity control	2 every 90 min
Absorption coefficient	44.4 cm^{-1}
Solution and refinement	
Solution mode	Patterson and Fourier and difference Fourier synthesis
Refinement mode	least-squares on F, observed reflex only
Final shift/error	0.03 average
Parameters: n variables	303
w scheme	empirical such as to give no trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle F_o\rangle$ or $\langle \sin\theta/\lambda\rangle$ [10]
ΔF final	0.85, −1.02 e Å^{-3}
R, R_w	0.081, 0.082
Atomic factors	neutral atoms: International Tables for X-ray Crystallography. Anomalous dispersion applied for Rh, P, Cl and F [12]
Programs and computer	VAX 11/750, XRAY 80 [8], DIFABS [9], PESOS [10], PARST [11]

ities of the R-DABR′, PR_3-ligands. The size of R and R′ substituents plays an important role in the stability and reactivity of these hydrides.

Electronic and steric factors determine the length of Rh–^{1}H bond which causes the shift of ν(Rh–H) towards higher or lower frequencies. In accordance with our results (Table III), we have found that for the same phosphine ligand, the ν(Rh–H) vibrations shift to lower frequencies when the π acceptor ability of the R-DAB ligand increases, (for comparison we have included the data for the bipy ligand). The shift of ν(Rh–H) frequency toward higher values is accompanied by a decrease in the electronic density of the metallic atom and therefore by less back donation of the metal towards the ligand.

The relationship between ν(Rh–H) frequencies and the basicity of tertiary phosphine ligands has been studied in rhodium–hydride–tertiary phosphine complexes [13].

The inductive effect of 1,4 substituents in R-DAB ligands (RN=CR′CR′=NR) follows the trend $CH_3 <$ c-Hex < t-but, and for the steric effect the order found is: $CH_3 <$ i-pr < t-but < c-Hex [6]. This in general agrees with our results.

The greatest steric impediment is shown by the ligand t-but-DAB and we have observed that compounds with this ligand have the highest ν(Rh–H) frequencies for any phosphine.

When we studied the ν(C=N) frequency we found a sequence similar to the ν(Rh–H) one (Table III). We have found that ν(C=N) increases when PR_3 basicity increases: $PEt_3 > PMePh_2 > PPh_3$. Those complexes with arylic-*p*-substituted phosphine $P(p\text{-}C_6H_4F)_3$ present a ν(C=N) similar to the compound with alkyl-phosphine.

^{1}H NMR Spectroscopy

Table II summarizes ^{1}H NMR data of the complexes. The high field hydride resonance, with intensity corresponding to two protons, has the appearance of a quartet, in agreement with two equivalent hydride-hydrogens coupled to the rhodium and to the two phosphorus nuclei, with very similar J values, $^2J(\text{H–P}) \simeq {}^1J(\text{H–Rh})$ [14, 15]. The hydride signal appears in the −15 to −17 ppm region; when the R-DAB changes, there is no noticeable shift of the signal, only compounds with t-but-DAB ligand present a shift to higher field.

TABLE II. IR and ^1H NMR Spectroscopic Data for $[RhH_2(R\text{-}DAB)(PR'_3)_2]^+$ Complexes

Compound		IR $\nu(Rh-H)$ (cm^{-1})	Chemical shifts δ (ppm) from TMS in $CDCl_3$[a]							
			Hydride		R-DAB				Phosphine	
			δ (ppm)	J (Hz)	H-imine		c-Hex		δ (ppm)	Δ*
					δ (ppm)	Δ	δ (ppm)	Δ		
I	$[RhH_2(c\text{-}Hex\text{-}DAB)(PPh_3)_2]^{+\,b}$	2080w 2060m	−15.6(m,2H) −16.1(m,2H)	15 13	8.3(s,2H)	0.36	1a = 3.2(t,2H) CH_2 = 2−1(m,20H)	0.03	(o,m,p) = 7.40(m,30H)	0.10
II	$[RhH_2(c\text{-}Hex\text{-}DAB)\{p(C_6H_4F)_3\}_2]^+$	2180m 2080m	−15.88(q,2H)	14.2	8.45(s,2H) 8.42	0.51	1a = 2.74(t,2H) 2e = 6e = 1.33 3e = 5e ≃ 4e = 0.75 2a, 6a, 3a 5a, 4a 0.61	−0.43 −0.49 −0.95 −0.50	(o) = 7.24(m,12H) (m) = 7.12(m,12H)	−0.02 0.12
III	$[RhH_2(c\text{-}Hex\text{-}DAB)(PMePh_2)_2]^+$	2060m	−15.97(q,2H)	16	8.45(s,2H)	0.51	1a = 2.73(t,2H) 2e = 6e 1.47 3e = 5e ≃ 4e = 1.41 2a, 6a, 3a 5a, 4a 0.77	−0.44 −0.34 −0.3 −0.5	(CH_3) = 1.96(s,6H) (o,m,p) = 7.44(m,20H)	0.28 −0.33 0.07
IV	$[RhH_2(c\text{-}Hex\text{-}DAB)(PEt_3)_2]^{+\,b}$	2080sh 2060m	−17.12(q,2H)	17	8.47(s,2H)	0.53	1a = 3.71(t,2H) 2e = 6e = 2.09 3e = 5e = 1.90 4e = 1.70 2a, 6a = 1.40−1.60 3a, 5a 4a 1.15−1.40	0.54 0.27 0.20 0 0 0	(CH_3) = 0.97(m,18H) (CH_2) = 1.56(t,12H)	−0.08 0.18
					CH_3-imine		NH_2			
V	$[RhH_2\{NH_2\text{-}DAB(CH_3,CH_3)\}(PPh_3)_2]^+$	2090w 2060m	−15.58(q,2H)	14	1.39(s,6H)	−0.58	5.19(s,4H)	−0.14	o = 7.59(m,12H) $m+p$ = 7.43(m,18H)	0.25 0.09
VI	$[RhH_2\{NH_2\text{-}DAB(CH_3,CH_3)\}\{P\text{-}(p\text{-}C_6H_4F)_3\}_2]$	2120w 2040m	−15.70(q,2H)	14.3	1.49(s,6H)	−0.48	5.38(s,4H)	0.05	o = 7.56(m,12H) m = 7.15(m,12H)	0.3 0.15
VII	$[RhH_2\{NH_2\text{-}DAB(CH_3,CH_3)\}(PMePh_2)_2]^+$	2080w 2060m	−16.03(q,2H)	16.4	1.44(s,2H)	−0.53	5.46(s,4H)	0.13	CH_3 = 2.08(s,6H) o = 7.50(m,8H) $m+p$ = 7.39(s,12H)	0.41 0.03 0.02

VIII	$[RhH_2\{NH_2\text{-}DAB(CH_3,CH_3)\}(PEt_3)_2]^+$	2040m	−17.23(q,2H)	18.1	2.11(s,6H)	0.14	5.98(s,4H)	0.65	CH_3 = 1.19(m,18H) CH_2 = 1.63(m,12H)	−0.14 0.24
					H-imine		t-But			
IX	$[RhH_2(t\text{-}Bu\text{-}DAB)(PPh_3)_2]^+$	2180w 2120m	−16.09(q,2H)	13.86	8.66(s,2H)	0.73	1.59(s,18H)	0.29	$m+p$ = 7.45(m,18H) o = 7.37(m,12H)	0.11 0.03
X	$[RhH_2(t\text{-}Bu\text{-}DAB)\{P(p\text{-}C_6H_4F)_3\}_2]^+$	2060m	−15.89(q,2H)	14.1	8.64(s,2H)	0.75	1.62(s,18H)	0.32	o = 7.50(m,12H) m = 7.01(m,12H)	0.24 0.01
XI	$[RhH_2(t\text{-}Bu\text{-}DAB)(PMePh_2)_2]^+$	2100w 2080m	−16.22(q,2H)	16.58	8.73(s,2H)	0.80	0.79(s,18H)	−0.59	o,m,p = 7.44(m,20H) CH_3 = 2.06(s,6H)	0.07−0.03 0.38
XII	$[RhH_2(t\text{-}Bu\text{-}DAB)(PEt_3)_2]^+$	2140w 2060m	−17.62(q,2H)	18.0	8.75(s,2H)	0.82	1.01(s,18H)	−0.29	CH_2 = 1.57(t,12H) CH_3 = 0.99(m,18H)	0.18 −0.06

[a]Multiplicity, number of protons; $\Delta = \delta_{complex} - \delta_{ligand}$. [b]These compounds are described in part I, and are consigned here for comparison.

A noticeable shift upfield has been observed when the phosphine basicity increases (Table II): $PEt_3 > PMePh_2 > P(p\text{-}C_6H_4F)_3 > PPh_3$.

The integrated intensities from the rest of the ^1H resonances evidence the existence of two phosphine and one R-DAB ligand in every complex, which agrees with the elemental analysis data.

An indication that R-DAB is symmetrically coordinated to the metal by the two nitrogen atoms, σ,σ,-N,N′ (4), is that only one signal from the imine protons of Ph–DAB, c-Hex–DAB, t-but–DAB and the methyl protons of the NH_2R–$DAB(CH_3,CH_3)$ ligands, was seen in the spectra. The occurrence of two signals could induce us to think of an asymmetric coordination; however after we solved the structure of some of these compounds we found that interactions with the ClO_4^- anion may cause the appearance of two signals instead of one.

Δ values (Table II) let us know if proton signals shift to higher or lower field upon coordination. The study of Δ values for different phosphines and R-DAB ligands was done in Part I [1].

^{31}P NMR Spectroscopy

To confirm the structural data obtained from ^1H NMR, ^{31}P NMR spectra were run for some of the complexes, Table IV. Apart from the PF_6^- signals (in those complexes having the PF_6^- anion) only one phosphine resonance, a doublet due to its coupling to Rh, was seen in the ^{31}P spectra (−200 to 200 ppm region), which confirms the existence of a symmetric environment around the Rh atom. Selectively decoupling all protons except the hydride ones, each line of the doublet splits into three, which indicates that two protons are coupled to the phosphorus nuclei with identical ^3J(P–Rh–H) values. This gives support to the ^1H NMR conclusions about the distribution of ligands. To find out if the phosphine ligands are *cis* or *trans* the resolution of the structure of two of these hydrides, chosen at random, has demonstrated that the phosphines are *trans* to each other.

Molecular Structure of $[RhH_2(c\text{-}Hex\text{-}DAB)\{P(p\text{-}C_6H_4F)_3\}_2]ClO_4$ (A)

The molecular geometry of A, is depicted together with the atomic numbering in Fig. 1. Perchlorate anion and hydrogen atoms do not appear for clarity. The atomic coordinates and equivalent isotropic temperature factors, with estimated standard deviations are consigned in Table V; bond lengths and angles around the rhodium are given in Table VI. The complex crystallizes as yellow prisms, with orthorhombic symmetry, space group *Pbnm*, with four molecules per unit cell, with a = 13.032(1), b = 18.166(2), c = 21.449(2) Å, Z = 4, V = 5077.8(8) and D_c = 1.37 g cm^{-3}, Table I. The Rh(III) has a distorted octahedral coordination, in which a

TABLE III. IR ν(Rh–H) and ν(C=N) Stretching Frequencies (cm^{-1}) of [RhH_2(R-DAB)(PPh_3)$_2$]$^+$ [a]

R-DABR′	ph-DAB	c-Hex-DAB	$NH_2DAB(CH_3CH_3)$	t-but-DAB	bipy
ν(Rh–H)	2060 2040	2080 2060	2090w 2060m	2180w 2120m	2135 2080
ν(C=N)	1590	1600w	1600	1620	

[a] KBr disks.

TABLE IV. ^{31}P Chemical Shifts of [RhH_2(R-DAB)(PR_3)$_2$]$^+$ in Cl_3DC[a]

Compound	Phosphine		Δ* [b]	PF_6^-	
[RhH_2(Ph-DAB)(PPh_3)$_2$]PF_6	41.97	^1JP,Rh = 115 Hz	47.13	−143.8	^1JP,F = 714 Hz
[RhH_2{NH_2-DAB(CH_3,CH_3)}(PPh_3)$_2$]ClO_4	46.57	^1JP,Rh = 114 Hz ^2JP,H = 13 Hz	51.73		
[RhH_2(c-Hex-DAB)($PMePh_2$)]ClO_4	19.99	^1JP,Rh = 114 Hz ^2JP,H = 15 Hz	46.36		
[RhH_2(c-Hex-DAB)(PEt_3)$_2$]PF_6	23.64	^1JP,Rh = 110 Hz ^2JP,H = 16 Hz	41.99	−143.9	^1JP,F = 714 Hz

[a] ppm (85% H_3PO_4). [b] Δ* $\delta_{complex} - \delta_{free\ ligand}$·

TABLE V. Atomic Parameters for [RhH_2(c-Hex-DAB){P(p-C_6H_4F)$_3$}$_2$]ClO_4

Atom[a]	x/a	y/b	z/c	U_{eq}[b]
Rh1	0.0006(1)	0.1845(0)	0.2500(0)	47(0)
P1	−0.0167(2)	0.2086(1)	0.1454(1)	51(1)
F1	0.0972(9)	0.5133(4)	0.0751(4)	148(5)
C111	0.0174(7)	0.3028(5)	0.1236(4)	57(3)
C112	−0.0402(9)	0.3435(6)	0.0828(5)	78(4)
C113	−0.0135(13)	0.4137(7)	0.0665(6)	98(6)
C114	0.0714(15)	0.4437(6)	0.0913(7)	103(6)
C115	0.1335(12)	0.4048(7)	0.1301(7)	105(6)
C116	0.1052(10)	0.3348(6)	0.1476(6)	83(5)
F2	−0.4468(8)	0.1763(7)	0.0606(5)	177(6)
C121	−0.1475(9)	0.1988(6)	0.1175(5)	70(4)
C122	−0.2258(9)	0.2263(8)	0.1525(5)	89(5)
C123	−0.3295(10)	0.2216(11)	0.1323(7)	123(7)
C124	−0.3466(13)	0.1834(10)	0.0788(8)	124(7)
C125	−0.2732(14)	0.1550(9)	0.0428(8)	116(7)
C126	−0.1722(11)	0.1658(7)	0.0595(7)	103(5)
F3	0.2222(10)	0.0228(6)	−0.0286(5)	177(6)
C131	0.0591(8)	0.1523(5)	0.0906(4)	61(3)
C132	0.1207(16)	0.1829(8)	0.0499(9)	162(9)
C133	0.1751(19)	0.1389(10)	0.0085(10)	206(12)
C134	0.1653(13)	0.0659(8)	0.0114(7)	114(7)
C135	0.1076(11)	0.0332(7)	0.0526(7)	89(5)
C136	0.0525(9)	0.0782(6)	0.0920(6)	79(4)
N3	0.1264(8)	0.1113(6)	0.2500(0)	58(4)
C31	0.2370(11)	0.1362(9)	0.2500(0)	74(6)
C32	0.2863(15)	0.1186(19)	0.1944(9)	250(17)
C33	0.4019(17)	0.1438(20)	0.1971(9)	222(18)
C34	0.4467(19)	0.1205(14)	0.2500(0)	183(25)
N2	−0.0687(8)	0.0734(6)	0.2500(0)	55(4)
C21	−0.1794(11)	0.0554(8)	0.2500(0)	65(5)
C22	−0.2055(9)	0.0105(7)	0.1922(6)	90(5)
C23	−0.3186(12)	−0.0091(10)	0.1917(9)	144(9)
C24	−0.3447(16)	−0.0519(15)	0.2500(0)	175(15)
C1	0.0018(14)	0.0241(8)	0.2500(0)	89(7)
C2	0.1080(12)	0.0421(8)	0.2500(0)	89(8)
Cl1*	0.4034(9)	0.3497(5)	0.1889(7)	171(0)
O1	0.3355(14)	0.3639(8)	0.2500(0)	171(0)
O2*	0.3619(20)	0.2973(12)	0.1483(15)	171(0)
O3*	0.4175(19)	0.4083(12)	0.1534(15)	171(0)
O4*	0.4871(19)	0.3323(10)	0.2162(13)	171(0)

[a] Starred items: occupancy factor 0.5. [b] Thermal parameters as: $U_{eq} = (1/3)\Sigma[U_{ij}a_i^*a_j^*a_ia_j\cos(a_i,a_j)10^4]$.

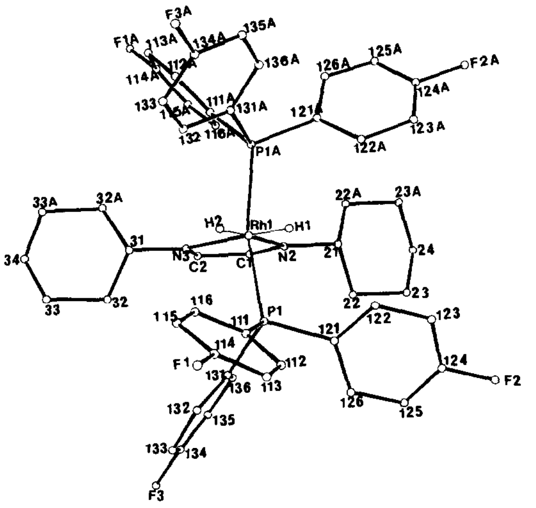

Fig. 1. ORTEP drawing of the [RhH_2(c-Hex-DAB){P(p-C_6H_4F)$_3$}$_2$]$^+$ cation.

TABLE VI. Selected Bond Distances and Angles for [RhH$_2$(c-Hex-DAB){P(*p*-C$_6$H$_4$F)$_3$}$_2$]ClO$_4$

Bond distances (Å)			
Rh(1)–P(1)	2.297(2)	Rh(1)–N(2)	2.211(11)
Rh(1)–N(3)	2.116(11)	P(1)–C(111)	1.829(9)
P(1)–C(121)	1.816(11)	P(1)–C(131)	1.845(10)
N(2)–C(1)	1.284(20)	N(3)–C(2)	1.280(19)
N(2)–C(21)	1.479(18)	N(3)–C(31)	1.511(18)
C(1)–C(2)	1.422(24)		
Bond angles (°)			
N(2)–Rh(1)–N(3)	75.1(3)	N(2)–Rh(1)–P(1)	97.7(1)
N(3)–Rh(1)–P(1)	101.3(1)	N(2)–Rh(1)–H(1)	95.0(2)
N(2)–Rh(1)–H(2)	174.5(2)	N(3)–Rh(1)–H(1)	170.1(3)
N(3)–Rh(1)–H(2)	99.4(2)	P(1)–Rh(1)–H(1)	79.7(1)
P(1)–Rh(1)–H(2)	83.3(1)	H(1)–Rh(1)–H(2)	90.5(1)
P(1)–Rh(1)–P(1)	155.3(1)	N(2)–C(1)–C(2)	122.5(12)
N(3)–C(2)–C(1)	114.0(11)		

c-Hex–DAB ligand is σ,σ-N,N′ chelated. The two phosphine ligands are *trans* and the two hydride-hydrogens are in *cis* position. The cyclohexyl rings on both imine N-atoms are in the chair conformation with normal C–C distances and bond angles. Atoms $Rh^1C^1C^2N^2N^3C^{21}C^{24}C^{31}C^{34}$ are in special positions and in the equatorial plane of the molecule, the distance Rh–P (the same for both P atoms, because of the molecular symmetry) is normal for Rh(III) complexes, 2.297(2) Å but compared with those observed in compound [RhH$_2$(ph-DAB)(PPh$_3$)$_2$]-PF$_6$ (**B**) [5], 2.320(4), 2.315(3), it is noticeably shorter. In complex **A**, both phosphines, in a *trans* position, bend towards the two hydrogen-hydride atoms making an angle P^1RhP^{1A} of 155.3(1)°. For complex **B**, the angle P^1RhP^2 is 164.9(4)°.

If one compares distances and angles in the metallocycle $N^2{=}C^1C^2{=}N^3$–Rh, for the two different R-DAB ligands, ph-DAB and c-Hex-DAB, complexes **A** and **B**, we find that C=N distances are practically the same: ph-DAB; 1.277(16), 1.275(19); c-Hex-DAB, 1.284(20), 1.280(19), but a remarkable difference in the C^1–C^2 bond length and NRhN′ angle has been observed: C^1–C^2 = 1.487(20), NRhN′ = 77.2(4)° for ph–DAB and C^1–C^2 = 1.422(24), NRhN′ = 75.1(3)° for c-Hex-DAB. This implies an opening of the metallocycle heterodiene ring when the π acceptor capacity of the ligand increases, (phen-DAB > c-Hex-DAB).

The delocalization of charge produced by the aromatic ring (ph-DAB), complex **B**, may be responsible for the shortening of bond lengths N^2–C^{21}, N^1–C^{11}, 1.415(17), 1.419(16) compared with N^2–C^{21}, N^3–C^{31}, 1.479(18), 1.511(18) for c-Hex-DAB, complex **A**. As expected the $N^3{=}C^2$–$C^1{=}N^2$ skeleton is essentially planar.

Atoms $C^{32}C^{33}C^{34}C^{24}$ and the six fluorine atoms of the phosphine ligands show a big thermal vibration, the same as ClO$_4^-$ anion; O^1 of ClO$_4^-$ anion is in a special position and Cl, O^2, O^3, O^4 in a general position with a population factor of 50%. Further refinement has not been possible because of the mentioned thermal vibration.

In addition it is interesting to note that oxygens of the perchlorate anion present interactions with some carbon atoms of the complex cation, C^2–O^1 (3.32(2) Å); C^{33}–O^2 (3.02(4) Å) and C^{35}–O^3 (2.15(3) Å). We have found this already with other compounds having a ClO$_4^-$ anion [5]; the interaction of any of the oxygens of ClO$_4^-$ with an imine carbon, C^2–O^1 in this case, seems to be responsible for the double signal that the imine proton gives in the ^{1}H NMR spectra. The imine proton resonance for the R-DAB ligand, σ,σ-N,N′ coordinated, would be a singlet. As it seems to be unlikely that this connection, in the crystalline state, remains in Cl$_3$DC solution we tried to make the ^{1}H NMR spectrum in the solid, but a very small amount of Rh^{2+} makes it impossible to get a reasonable spectrum. Anions PF$_6^-$ have not presented this sort of 'anion–cation' interaction and the imine proton signal has been always a singlet. An explanation for this may be that these complexes are not dissociated in solution on the NMR time scale.

Supplementary Material

Available on request from the authors.

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