Synthesis and Characterization of New Cationic Hydride Complexes of Rhodium(III)

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Abstract

New cationic hydride complexes of rhodium(III) with PR_3 and R-DAB ligands have been prepared and characterised. The tertiary phosphines employed were PPh_3, $PMePh_2$, PEt_3 and the R-DAB ligands, (RN:CR'CR':NR), c-Hex-DAB, Ph-DAB, NH_2-DAB-(CH_3,CH_3). Hexacoordinate-dihydride complexes, characterized by ^1H and ^{31}P NMR, with stoichiometry $[RhH_2(R\text{-}DAB)(PR_3)_2]X$ were obtained. Compounds with other stoichiometries (R-DAB/PR_3 = 1 or 2) are also possible. Preliminary studies of the catalytic activity in hydrogenation of olefins have been carried out.

Introduction

The synthesis and reactivity of some hydride complexes of rhodium with phosphine and conjugated chelating ligands such as 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) have been reported in the literature [1]. The tertiary phosphine stabilizes the metal–hydrogen bond and the chelate stabilizes σ-metal–carbon bond. As far as we know, no complexes of rhodium with phosphine and α-diimines (R-DAB) as ligands have been reported. Analogous ruthenium compounds are described in the literature [2].

Diazabutadiene ligands, R-DAB, of general formula RN:CR'CR':NR, have attracted much attention during the past few years in view of their versatile bonding properties and chemical reactivity when coordinated to a metal. These ligands are basic but also have a strong π-back bonding capability, due to their good σ-donor, π-acceptor characteristics; they can act as a monodentate, bidentate or bridging ligands. The type of behaviour depends on the metal, the other ligands and particularly on the steric and electronic characteristics of R and R' on the ligand. Herein they will be referred to as R-DAB when they are derivatives of glioxal or as R-DAB (CH_3,CH_3) when they derive from diacetyl [3].

In this paper we describe the synthesis and NMR characterization of dihydrides of general formula

$$[RhH_2(R\text{-}DAB)(PR_3)_n]X$$

n = 1,2; X = ClO_4^-, PF_6^-; R-DAB = c-Hex-DAB, Ph-DAB, NH_2-DAB (CH_3,CH_3); PR_3 = PPh_3, $PMePh_2$, PEt_3. We chose the complexes [Rh(R-DAB)(COD)]X as starting compounds. These hydrides are potential catalysts in hydrogenation of olefins. Their reactivity will be described in a separate paper.

Experimental

Reagent grade commercial starting materials were used without further purification. Solvents were carefully dried, purified and degassed before use. All manipulations were carried out using Schlenk techniques, at room temperature.

The diazadiene ligands were prepared according to published method, [4] by adding 2 equivalents of amine to glioxal (aqueous solution) or diacetyl into hydrazine (aqueous solution), at 0 °C.

Preparation of the Compounds

Synthesis of [Rh^I(R-DAB)COD]X (A) (X^- = ClO_4^-, PF_6^-; DAB = c-Hex-DAB, Ph-DAB, NH_2-DAB(CH_3,CH_3))

The R-DAB ligand (3 mmol) is added to a suspension of $[RhCODCl]_2$ (1 mmol), in 30 ml methanol. On addition of an aqueous solution of the sodium salt of the anion the complex precipitates. It recrystallizes from hot methanol and diethyl ether. The

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colour of the complexes varies with the substituents on the R-DAB ligand: olive green for Ph-DAB, dark green for c-Hex-DAB and red for NH_2-DAB.

Synthesis of [RhH_2(R-DAB)(PR_3)$_2$] X (B)

A solution of the phosphine (1.5 mmol) in ethyl ether was added to a solution (15 ml) of A (0.5 mmol) in methanol and molecular hydrogen was bubbled through during 3 h. After that the solution becomes yellow to brown, depending on the ligands. A solid was precipitated by addition of an aqueous solution of $NaClO_4$ or NH_4PF_6 and partial evaporation of the solvent and recrystallized from methanol–ethyl ether. Yield 70–80%.

Synthesis of [RhH_2(R-DAB)PR_3] X (C)

The filtrate, after separation of the 6-coordinate hydride, is hydrogenated again and more anion is added (ClO_4^-, PF_6^-). The solid was obtained by precipitation with ethyl ether and dried under vacuum. These compounds can also be obtained by using a smaller amount of phosphine than was used in the previous synthesis. Yield 20–25%.

Techniques

Microanalyses were performed at the Department of Inorganic Chemistry of Alcalá de Henares University (Madrid). 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 16 000 Hz and 32 K data points were necessary to observe 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 (31 000 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 simultaneously decouple aliphatic and aromatic ligand resonances but not the hydride signals, which appear well separated ~15 ppm upfield from TMS.

Results and Discussion

As starting material we chose [Rh^I(R-DAB)COD] X (A) easily made by treating [Rh^I(COD)Cl]$_2$ in methanol with an excess of R-DAB, followed by the addition of a voluminous, non-coordinating anion (Scheme 1).

$$RhCl_3\cdot 3H_2O \xrightarrow[EtOH]{COD} [Rh^I(COD)Cl]_2 \xrightarrow[MetOH]{R\text{-}DAB+X^-} [Rh^I(R\text{-}DAB)COD]X$$

A

$$[Rh^I(R\text{-}DAB)COD]X \xrightarrow[H_2]{PR_3} [RhH_2(R\text{-}DAB)(PR_3)_2]X$$

A B

Scheme 1. X = ClO_4^-, PF_6^-

Complex **A** is a coordinatively unsaturated 16 e Rh(I) compound, which is useful for the synthesis of new cationic derivatives. It reacts with an excess of PR_3 in a hydrogen atmosphere at room temperature to give dihydrides of general formula [RhH_2(R-DAB)(PR_3)$_2$] X (**B**). These dihydrides (**I, II, III, IV, V**) are stable in air, soluble in polar solvents and electrolytes 1:1, as expected. Their physical properties and analytical data are shown in Table I.

Another type of complexes (**VI, VII, VIII**) with different properties is obtained with the proportion R-DAB/PR_3 = 1; they are insoluble in $CDCl_3$ which makes their characterization by NMR impossible, but in accordance with their analytical data we tentatively have supposed them to be pentacoordinated [5, 6].

In presence of a large excess of DAB, stoichiometries R-DAB/PR_3 2/1 are obtained, **IX**. If the experiment is carried out with shortage of R-DAB, phosphine hydride-complexes are obtained, **X**, [7].

The colour of the compounds is more intense when the proportion of DAB is greater; thus the complexes of formula [RhH_2(R-DAB)(PR_3)$_2$] X are in the range of yellow, while those of formula [RhH_2(R-DAB)PR_3] X and [RhH_2(R-DAB)$_2PR_3$] X are brown.

Infrared Spectra

The IR spectra, Table I, show weak to medium absorption bands, in the range 2140–2010 cm^{-1} due to ν(Rh–H) plus the characteristics bands of R-DAB and phosphine ligands.

^{1}H and ^{31}P NMR Spectra

Table II summarizes ^{1}H NMR data of the complexes examined here. All of them showed a signal (with intensity corresponding to two protons) in the –15 to –17 ppm region of the spectrum that can be readily assigned to the hydride protons (see Fig. 2a). The integrated intensities from the rest of ^{1}H resonances evidence the existence of two phosphines and one DAB ligand in every complex, which agrees with elemental analysis data. Only one signal from the imine protons of DAB and methyl protons of

TABLE I. Analytical and Physical Data for the New Rhodium Complexes

Compound		Λ[a] (ohm^{-1} cm^2 mol^{-1})	Colour	Analysis: found (calculated) (%)			Infrared ν(Rh- H) (cm^{-1})	λ (nm) (ϵ $l\,mol^{-1}$)
(I)	$[RhH_2(c\text{-Hex-DAB})(PPh_3)_2]PF_6$	125	Yellow	60.1	5.9	2.7	2020br	340 (2884)
				(60.5)	(5.6)	(2.8)		
(II)	$[RhH_2(ph\text{-DAB})(PPh_3)_2]ClO_4$	150	Light beige	64.0	4.8	2.8	2030m	415 (2536)
				(64.1)	(4.7)	(3.0)		355 (2965)
(III)	$[RhH_2(NH_2\text{-DAB}(CH_3CH_3))(PPh_3)_2]ClO_4$	120	Yellow	56.8	5.1	6.5	2090sh	480 (2023)
				(57.0)	(5.0)	(6.6)	2060m	400 (2427)
								345 (2814)
(IV)	$[RhH_2(c\text{-Hex-DAB})(PMePh_2)_2]ClO_4$	116	Yellow	58.0	6.0	3.3	2060m	355(4283)
				(58.2)	(6.2)	(3.4)		
(V)	$[RhH_2(c\text{-Hex-DAB})(PEt_3)_2]PF_6$	129	Orange	44.0	8.1	4.0	2060m	405 (4099)
				(44.2)	(7.9)	(4.0)	2080sh	
(VI)	$[RhH_2(c\text{-Hex-DAB})(PPh_3)]Cl$	110	Brown	61.9	6.8	4.3	2140m	405 (2720)
				(61.7)	(6.6)	(4.5)	2060sh	340 (2950)
(VII)	$[RhH_2(ph\text{-DAB})(PPh_3)]ClO_4$	199	Brown	56.5	4.4	4.2	2050sh	400 (2662)
				(56.9)	(4.3)	(4.2)	2010m	350 (3045)
(VIII)	$[RhH_2(NH_2\text{-DAB}(CH_3CH_3))(PPh_3)]ClO_4$	114	Brown	45.0	4.3	9.5	2100m	400 (4414)
				(45.6)	(4.3)	(9.6)		370 (4343)
(IX)	$[RhH(c\text{-Hex-DAB})_2(PPh_3)]PF_6$	140	Brown	58.5	6.6	5.7	2080m	415 (3050)
				(58.1)	(6.6)	(5.9)		360 (3300)
(X)	$[RhH_2(PPh_3)_4]PF_6$	125	Yellow	66.4	5.1	–	2260m	
				(66.4)	(4.8)	–	2130m	

[a]Molar conductance at 25 °C in degassed acetone (10^{-3} M solutions).

TABLE II. ^1H and ^{31}P NMR Data of the New Rhodium Complexes

Compound	Chemical shift δ (ppm) from TMS in $CDCl_3$[a]					
	Hydride	Imino groups	Other resonances of R-DAB ligands		Phosphine resonances	
					^1H	^{31}P[j]
(I) $[RhH_2(c\text{-Hex-DAB})(PPh_3)_2]PF_6$	−15.6 (m,2H,15) −16.1 (m,2H,13)	8.3 (s,2H)	3.2 (t,2H)[b]	2–1 (m,20H)[e]	7.40 (m,30H)	
(II) $[RhH_2(Ph\text{-DAB})(PPh_3)_2]ClO_4$	−15.35 (q,2H,14)	8.50 (s,2H)	7.13 (t,2H)[d] 6.91 (d,4H) 6.72 (d,4H)		7.30 (m,30H)	41.97 (d,115)
(III) $[RhH_2(NH_2\text{-DAB}(CH_3,CH_3))(PPh_3)_2]ClO_4$	−15.58 (q,2H,14)		1.39 (s,6H)[e]	5.19 (s,4H)[f]	7.59 (m,12H)	7.43 (m,18H)
(IV) $[RhH_2(c\text{-Hex-DAB})(PMePh_2)_2]ClO_4$	−15.97 (q,2H,16)	8.45 (s,2H)	2.73 (t,2H)[b]	1.5–0.8 (m,20H)[c]	1.96 (s,6H)[g]	7.44 (m, 20H)
(V) $[RhH_2(c\text{-Hex-DAB})(PEt_3)_2]PF_6$	−17.12 (q,2H,17)	8.47 (s,2H)	3.71 (t,2H)[b]	2.1–1.15 (m,20H)[c]	0.97 (s,18H)[h]	1.56 (t,12H)[i] 23.64 (d,111)

[a]Multiplicity, number of protons and values of $^2J(H,P) \simeq {}^1J(H,Rh)$ in Hz are given in parentheses. [b]δ(CH) of c-Hex-DAB. [c]δ(CH_2) of c-Hex-DAB. [d]Aromatic protons of Ph–DAB. [e]Methyl groups of NH_2–DAB(CH_3,CH_3). [f]δ(NH_2) of NH_2–DAB(CH_3,CH_3). [g]δ(CH_3) of $PCH_3(C_6H_5)_2$. [h]δ(CH_3) of $P(CH_2,CH_3)_3$. [i]δ(CH_2) of $P(CH_2,CH_3)_3$. [j] $^1J(P,Rh)$ in Hz in parentheses.

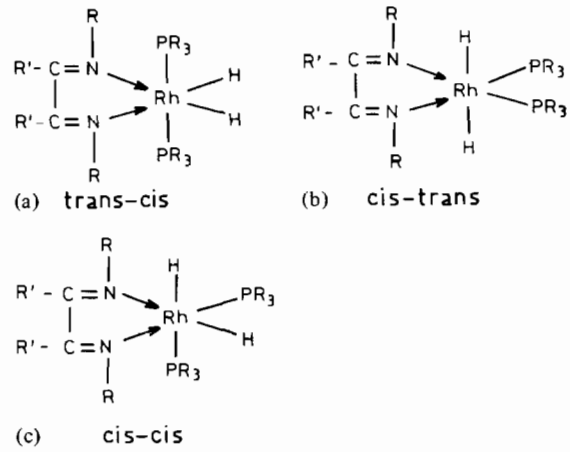


Fig. 1. Distribution of ligands around the Rh atom.

the NH_2-DAB(CH_3,CH_3) ligands was seen in the complexes, which is an indication that R-DAB is coordinated to the metal by the two nitrogen atoms. The only possible structures that agree with these data are depicted in Fig. 1. The presence of structure (c) (*cis–cis* isomer) can be readily excluded since, being asymmetric, it should give rise to two signals for the two hydride protons, which was not observed. The multiplicity of the hydride resonances, with the appearance of a quartet, is in agreement with structures (a) and (b) since both protons are equivalent, and they are coupled to the Rh atom and to the two phosphines, with very similar J values, $^2J(H–P) \simeq {}^1J(H–Rh)$ [8, 9].

Tables III and IV report the changes observed in the proton resonances of the ligands upon coordination. In absence of other effects, signals from protons close to the positively-charged metal ion are expected to shift downfield. This was in fact observed in complex **V** containing two aliphatic phosphines, where the CH from DAB, CH_2 from the phosphine and 1 ax, 2 eq and 6 eq cyclohexyl resonances shifted downfield to different extents. However, when aromatic phosphines are coordinating with Rhodium, through space aromatic ring currents, the effects on δ values of nearby protons are superimposed to the downfield effect above mentioned. In complex **IV**, which differs from complex **V** only in the type of phosphine ligand, signals from 1 ax, 2 eq, 6 eq cyclohexyl protons shifted in the opposite sense (upfield), which implies that ring current effects are dominating. The same situation was detected in the CH_3 and NH_2 proton resonances from DAB in complex **III** (see Table IV). Aromatic resonances from Rh–DAB shifted (upfield) upon coordination in complex **II**, most probably due also to ring current effects originated by the aromatic rings of the phosphines.

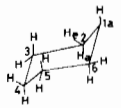
In order to confirm the structural data obtained from ^1H NMR, ^{31}P NMR spectra were run for some

TABLE III. ^{1}H NMR Parameters of Free and Coordinated Tertiary Phosphines

Complex		Phosphine	Free phosphine		Coordinated phosphine	
			δ (ppm)	J (Hz)	δ (ppm)	Δ (ppm)[a]
(II)	$[RhH_2(Ph\text{-}DAB)(PPh_3)_2]^+$	$P(C_6H_5)_3$	(*o,m,p*) = 7.34	^3J(H–P) = 10.5 - 11.5 ^4J(H–P) = 2.1 - 3.4	(*o,m.p*) = 7.30	–0.04
(III)	$[RhH_2(NH_2\text{-}DAB\text{-}CH_3,CH_3)(PPh_3)_2]^+$	$P(C_6H_5)_3$			(*o*) = 7.59	0.25
					(*m,p*) = 7.43	0.09
(IV)	$[RhH_2(c\text{-}Hex\text{-}DAB)(PMePh_2)_2]^+$	$PCH_3(C_6H_5)_2$	(CH_3) = 1.68	^2J(H–P) = 3.5 ^3J(H–P) = 7.5	(CH_3) = 1.96	0.28
			(*o*) = 7.47	^3J(*o,m*) = 7.5	(*o,m,p*) = 7.44	–0.03
			(*m* + *p*) = 7.37	^4J(*o,p*) = 1.5		0.07
(V)	$[RhH_2(c\text{-}Hex\text{-}DAB)(PEt_3)_2]^+$	$P(CH_2–CH_3)_3$	(CH_3) = 1.05	^2J(H–P) ≃ 0.5	(CH_3) = 0.97	–0.08
			(CH_2) = 1.39	^3J(H–P) = 14.1	(CH_2) = 1.56	0.18

[a] $\Delta = \delta_{complex} - \delta_{ligand}$.

TABLE IV. ^{1}H NMR Parameters of Free and Coordinated R-DAB Ligands (R′N=CRCR=NR′)

Complex		R-DAB	Free R-DAB		Coordinated R-DAB		
			δ (ppm)	J (Hz)	δ (ppm)	J (Hz)	Δ (ppm)[a]
(II)	$[RhH_2(Ph\text{-}DAB)(PPh_3)_2]^+$	$C_6H_5N{=}CHCH{=}NC_6H_5$[b]	CH = 4.85	$J(o,m)$ = 7.8	CH = 8.50		3.66
			o = 6.78	$J(m,p)$ = 7.4	*o* = 6.72	$J(o,m)$ = 7.5	–0.06
			m = 7.11		*m* = 6.91	$J(m,p)$ = 7.5	–0.19
			p = 6.12		*p* = 7.13		0.51
(III)	$[RhH_2(NH_2\text{-}DAB,CH_3,CH_3)(PPh_3)_2]^+$	$NH_2N{=}C(CH_3)C(CH_3){=}NNH_2$	CH_3 = 1.97		CH_3 = 1.39		–0.58
			NH_2 = 5.33		NH_2 = 5.19		–0.14
(IV)	$[RhH_2(c\text{-}Hex\text{-}DAB)(PMePh_2)_2]^+$	$C_6H_{11}N{=}CHCH{=}NC_6H_{11}$	CH = 7.94		CH = 8.45		0.51
			1a = 3.17	J(1a,2e) = J(1a,6e) = 4	1a = 2.73		–0.44
			2e = 6e = 1.82	J(1a,2a) = J(1a,6a) = 10.6	2e = 6e = 1.47		–0.34
			3e = 5e ≃4e = 1.70		3e = 5e ≃4e = 1.41		–0.3
			2a = 6a = 1.52		2a,6a,3a 5a,4a	0.77	–0.5
			3a = 5a = 1.35				
			4a = 1.23				
(V)	$[RhH_2(c\text{-}Hex\text{-}DAB)(PEt_3)_2]^+$	$C_6H_{11}N{=}CHCH{=}NC_6H_{11}$			CH = 8.47		0.53
					1a = 3.71		0.54
					2e = 6e = 2.09		0.27
					3e = 5e = 1.90		0.20
					4e = 1.70		0
					2a = 6a = 1.40–1.60		≃0
					3a,5a 4a	1.15–1.40	≃0

[a] $\Delta = \delta_{complex} - \delta_{ligand}$. [b] In DMSO; insoluble in other solvents.

of the complexes (see Table II). Apart from the PF_6^- signals, only one phosphine resonance (a doublet due to its coupling to Rh) was seen in the ^{31}P spectrum of each complex (−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, it can be seen Fig. 2) that each line of the doublet split into three, which indicates that two protons are coupled to the phosphorus nuclei with identical $^3J_{P-Rh-H}$ values. This gives additional support to a distribution of ligands in these Rh complexes, as depicted in structures (a) or (b). Either of these structures is compatible with the NMR data.

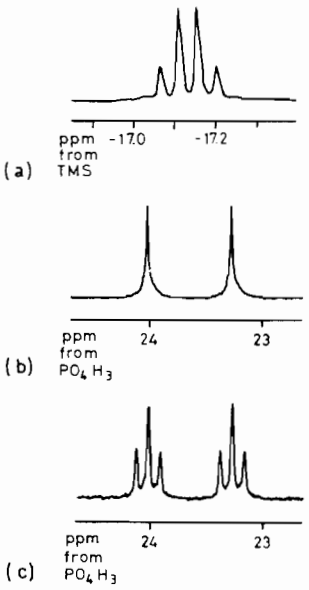


Fig. 2. NMR spectra of the $[RhH_2(c\text{-Hex-DAB})(PEt_3)_2]PF_6$ complex. (a) Hydride regions of the ^1H spectrum. (b) Broad band decoupled ^{31}P spectrum. (c) Selectively decoupled ^{31}P spectrum, showing $^3J_{P-Rh-H}$ residual couplings.

Preliminary X-ray work done on complex $[RhH_2(Ph\text{-DAB})(PPh_3)_2]PF_6$ indicates that the two phosphines are in *trans* position. Since the pattern of the hydride signals remain unchanged in the rest of hexacoordinated complexes as compared with that of the above complex, it seems reasonable to infer that its distribution of ligands around Rh (structure a) is maintained in the whole series of complexes.

In addition to the hydride quartet resonance, an additional set of hydride resonances of minor intensity has been detected in the spectrum of complex **I**. Signal-to-noise ratio was poor but two quintuplets ($J \simeq 15$ Hz) separated by 0.5 ppm could be seen in the spectrum. Such a pattern can be explained by the presence of minor amounts of the asymmetric isomer (c), that should give rise to two different signals for each hydride proton, the latter protons being coupled to four other nuclei (H, P, P and Rh) with similar J values.

The compounds **VI, VII, VIII** are rather insoluble in $CDCl_3$ and their spectra do not allow the establishment of any conclusion about the geometry of the molecules.

Catalytic Activity

We have carried out preliminary studies of the catalytic activity of the dihydride complexes obtained, studying the hydrogenation of 1-hexene in different reaction media (acetone, 2-methoxyethanol, acetone/$HClO_4$ 0.1 M), under 1 atm of H_2 using 1 ml of hexene and 6 mM of the complex. We have found that $[RhH_2(c\text{-Hex-DAB})(PPh_3)_2]PF_6$ gives the higher percentage of hexane (80%) in acetone after 1 h.

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References

1 C. Cocevar, G. Mestroni and C. Camus, *J. Organomet. Chem., 35,* 389 (1972).
2 B. Chaudret and R. Poilblanc, *J. Organomet. Chem., 204,* 115 (1981).
3 G. van Koten and K. Vrieze, *Adv. Organomet. Chem., 21,* 151 (1982).
4 H. Tom Dieck and W. Renk, *Chem. Ber., 104,* 110 (1971).
5 H. van der Poel, G. van Koten and K. Vrieze, *Inorg. Chim. Acta, 51,* 241 (1981).
6 H. van der Poel, G. van Koten and K. Vreize, *Inorg. Chim. Acta, 51,* 253 (1981).
7 L. M. Haines, *J. Organomet. Chem., 25,* C85 (1970).
8 T. Yoshida, T. Okano and S. Otsuka, *J. Am. Chem. Soc., 102,* 1967 (1980).
9 E. M. Hyde, J. D. Kennedy and B. L. Shaw, *J. Chem. Soc., Dalton Trans.,* 1571 (1977).