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Reactions of rhodium dihydride complexes $[RhH_2(R\text{-}DAB)(PR'_3)_2]^+$ with the acetylenes $CH_3OOCC{\equiv}CCOOCH_3$ and $HC{\equiv}CC_6H_5$. Crystal structure of $[\overline{RhC(CO_2CH_3)=C(CO_2CH_3)C(CO_2CH_3)=C}(CO_2CH_3)(C_6H_{11}N=CHCH=NC_6H_{11})\{PCH_3(C_6H_5)_2\}H_2O]ClO_4$

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Abstract

The products of the reactions between a series of rhodium *cis*-dihydrides cations $[RhH_2(R\text{-}DAB)(PR'_3)_2]^+$ (A) and the alkynes $CH_3OOCC{\equiv}CCOOCH_3$ (DMAD) and $HC{\equiv}CC_6H_5$ at room temperature and 40 °C (CH_2Cl_2 reflux) have been characterized by ^1H NMR, IR spectroscopy and elemental analysis. Hydrogen evolution was observed in all the reactions and there was no evidence of insertion of the alkyne into the Rh–H bond.

From DMAD compounds with a 1/1 ratio Rh/DMAD were obtained at room temperature but in refluxing CH_2Cl_2, H_2 and one molecule of phosphine are eliminated and two mols of DMAD incorporated to give, by dimerization of the acetylene, a metallocyclopentadiene complex. The molecular structure of one of these complexes $[\overline{RhC(CO_2CH_3)=C(CO_2CH_3)C(CO_2CH_3)=C}(CO_2CH_3)(c\text{-}Hex\text{-}DAB)PCH_3(C_6H_5)_2 \cdot H_2O]ClO_4$, is reported. This compound, an intermediate in the cyclotrimerization of alkynes, crystallizes in the monoclinic system, space group $P2_1/c$, unit cell dimensions: a 16.720(1), b 12.357(1), c 21.573(1) Å, β 106.53(1)°, $Z = 4$. The structure was resolved by Patterson and Fourier methods and refined to R and R_w values of 0.062 and 0.045 respectively.

Cyclotrimerization was observed in all the reactions of $HC{\equiv}CC_6H_5$ with **A** and crystals of composition $C_{24}H_{18}$, $(HC{\equiv}CC_6H_5)_3$, obtained. An intermediate com-

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pound, with a 1/2 ratio of $Rh/HC{\equiv}CC_6H_5$, with composition $[Rh\{NH_2\text{-}DAB.CH_3CH_3\}(HC{\equiv}CC_6H_5)_2P(C_6H_5)_3]^+[ClO_4]$ has also been isolated.

Introduction

Hydrides of transition metals generally react with olefins or acetylenes by insertion into the M–H bond; many examples can be found in the literature [2–4].

cis-Dihydride complexes behave differently when treated under mild conditions with π-acids, losing molecular hydrogen by reductive elimination and producing η^2-alkynes. With an excess of the acetylene under reflux, metallocyclopentadiene complexes can be obtained as a result of a cyclodimerization of the acetylene [5]. Reductive elimination of hydrogen from hydride complexes is favoured by the presence of a good π-acceptor ligand, which stabilizes the lower valent metal product through increased back-bonding [4,6]. Alkynes bearing electron-withdrawing substituents readily undergo cyclodimerization; the metallocyclopentadiene complexes are intermediates in the catalytic trimerization of alkynes to arenes [7,8].

cis-Dihydrides of transition metals have received considerable attention in recent years as catalysts for the hydrogenation of unsaturated organic molecules. Very little is known about catalytic reactions involving diazabutadiene complexes in which the diazabutadiene ligand R-DAB [1*] is not activated [9,10]. In binuclear complexes it has been seen that M-R-DAB systems in which the R-DAB is activated, are excellent precursors for the regiospecific cyclotrimerization of acetylenes [8,11,12].

As part of our research on cationic rhodium *cis*-dihydrides with diazabutadienes, R-DAB and phosphine ligands [13], of general formula $[RhH_2(R\text{-}DAB)R'(PR_3)_2]^+[X]^-$ (**A**) ($X = ClO_4, PF_6$) [1*], we report here our results on the reactions of such cations with the activated alkyne $CH_3OOCC{\equiv}CCOOCH_3$, DMAD, and the non activated $HC{\equiv}CC_6H_5$. The molecular structure of $[RhC(CO_2CH_3){=}C(CO_2CH_3)C(CO_2CH_3){=}C(CO_2CH_3)(C_6H_{11}N{=}CHCH{=}NC_6H_{11})\{PCH_3(C_6H_5)\}H_2O]ClO_4$ is also described.

Experimental

All reactions and manipulations were carried out under N_2 by Schlenk techniques, and at room temperature unless otherwise specified. Reagent grade commercial starting materials were used without purification. Solvents were carefully dried, purified, and degassed before use.

The ^1H 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 solution with a Philips 9501/01 Conductimeter. C, H and N, analyses were performed at the Inorganic Chemistry Department of Alcalá de Henares University (Madrid).

The syntheses of the salts $[RhH_2(R\text{-}DAB)(PR_3)_2]X$ (**A**) have been described previously [13].

(Continued on p. 93)

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* Reference numbers with asterisks indicate notes in the list of references.

Table 1

^1H NMR parameters of the products of reactions of $[RhH_2(R\text{-}DAB)(PR'_3)_2]X$ with DMAD [a]

Compound	R-DAB resonances				Phosphine resonances		CH_3(DMAD) resonances	
	c-Hex=CHCH=c-Hex							
	H imine	Δ	c-Hex	Δ		Δ		Δ
1 $[Rh(DMAD)(c\text{-}Hex\text{-}DAB)\text{-}\{P(p\text{-}C_6H_4F)_3\}_2][ClO_4]$	8.52 (s,2H)	0.58	1a 2.75 (t,2H)	−0.42	*o* 7.31 (m,12H)	0.05	3.90	0.04
			2e = 6e 1.44	−0.38	*m* 7.19 (m,12H)	0.19	3.86 6H	0.00
			3e = 5e	−0.26			3.83	−0.03
			4e 1.27	−0.43				
			2a = 6a 0.82	−0.7				
			3a = 5a 0.68	−0.67				
			4a	−0.55				
1' $[Rh(DMAD)_2(c\text{-}Hex\text{-}DAB)\text{-}\{P(p\text{-}C_6H_4F)_3\}][ClO_4]$	8.72 (s,1H)	0.78	1a 2.81 (t,2H)	−0.36	*o* 7.32 (m,6H)	0.06	3.83 (d,6H)	−0.03
	8.54 (s,1H)	0.6	2e = 6e 1.44	−0.38	*m* 7.19 (m,6H)	0.19	3.57 (d,6H)	−0.29
			3e = 5e = 4e 1.27	−0.43				
			2a = 6a 0.86	−0.66				
			3a = 5a 0.69	−0.66				
			4a	−0.54				
2 $[Rh(DMAD)(c\text{-}Hex\text{-}DAB)\{PPh_3\}_2][PF_6]$	8.45 (s,2H)	0.51	1a 2.72 (t,2H)	−0.45	*o,m,p* 7.48 (m,30H)	0.14	3.90 (br,6H)	0.04
			rest. 0.5–2					
2' $[Rh(DMAD)(c\text{-}Hex\text{-}DAB)\{PPh_3\}][PF_6]$	8.48 (s,1H)	0.54	1a 2.74 (t,2H)	−0.43	*m,p* 7.50 (m,9H)	0.16	3.63 (s,6H)	−0.23
	8.33 (d,1H)	0.39	2e = 6e 1.78	−0.04	*o* 7.39 (m,6H)	0.05	3.53 (s,6H)	−0.33
			3e = 5e = 4e 1.41	−0.29				
			2a = 6a 1.15–1.40	−0.22				
			3a = 5a 0.5–1	−0.60				
			4a					
3 $[Rh(DMAD)(c\text{-}Hex\text{-}DAB)\text{-}\{PMePh_2\}_2][ClO_4]$	8.45 (s,1H)	0.51	1a 2.72 (t,2H)	−0.45	CH_3 1.95 (s,6H)	0.27	3.80	−0.06
	8.39 (d,1H)	0.45	2e = 6e 1.48	−0.34	*o,m,p* 7.44 (m,20H)	0.02	3.71	−0.15
			3e = 5e = 4e 1.39	−0.31			3.67	−0.19
			2a,6a 0.78	−0.74				
			3a,5a	−0.55				
			4a	−0.45				

continued

Table I (continued)

3' [Rh(DMAD)$_2$(c-Hex-DAB)-(PMePh$_2$)][ClO$_4$]	8.38 (s,1H) 8.30 (d,1H)	0.44 0.36	1a 2.85 (t,2H) 2e = 6e 1.49 3e = 5e = 4e 1.40 2a,6a 3a,5a 0.63 4a	−0.32 −0.33 −0.30 −0.89 −0.72 −0.6	CH$_3$ 1.92 (s,3H) *o,m,p* 7.49 (m,10H)	0.24 0.07	3.80 3.70 12H 3.68	−0.06 −0.14 −0.20
	t-Bu=CHCH=t-Bu							
	CH imine	Δ	t-Bu	Δ				
6 [Rh(DMAD)(t-Bu-DAB)-{P(*p*-C$_6$H$_4$F)$_3$}][PF$_6$]	8.64 (s,2H)	0.75	0.56 (s,18H)	−0.74	*o* 7.50 (m,6H) *m* 7.01 (m,6H)	0.24 0.01	3.89 6H 3.80	0.03 −0.06
4 [Rh(DMAD)(t-Bu-DAB)(PPh$_3$)$_2$][ClO$_4$]	8.66 (s,2H)	0.73	0.59 (s,18H)	−0.71	*m* + *p* 7.45 (m,18H) *o* 7.37 (m,12H)	0.11 0.03	3.90 6H 3.78	0.04 −0.08
5 [Rh(DMAD)(t-Bu-DAB)-(PMePh$_2$)$_2$][ClO$_4$]	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	3.87 6H 3.76	0.01 −0.10
7 [Rh(DMAD)(t-Bu-DAB)(PEt$_3$)][PF$_6$]	8.75 (s,2H)	0.82	1.01 (s,18H)	−0.29	CH$_2$ 1.57 (m,6H) CH$_3$ 0.99 (m,9H)	0.18 −0.06	3.80 6H 3.68	−0.06 −0.18
	NH$_2$N=C(CH$_3$)C(CH$_3$)=NNH$_2$							
	(CH$_3$) imine	Δ	NH$_2$	Δ				
8 [Rh(DMAD)(NH$_2$-DAB-CH$_3$)-{P(*p*-C$_6$H$_4$F)$_3$}$_2$][ClO$_4$]	1.47 (s,6H)	−0.50	5.16 (s,4H)	−0.17	*o* 7.56 (m,6H) *m* 7.15 (m,6H)	0.3 0.15	3.92 3.79 6H 3.69	0.06 −0.07 −0.17
9 [Rh(DMAD)(NH$_2$-DAB-CH$_3$)-(PPh$_3$)$_2$][ClO$_4$]	1.40 (s,6H)	0.57	5.19 (s,4H)	−0.14	*o* 7.59 (m,12H) *m* + *p* 7.43 (m,18H)	0.25 0.09	3.89 6H 3.82	0.03 −0.04
9' [Rh(DMAD)(NH$_2$-DAB-CH$_3$)-(PPh$_3$)][ClO$_4$]	1.40 (s,3H) 1.26 (s,3H)	−0.57 −0.71	5.20 (s,4H)	−0.13	*o* 7.56 (m,6H) *m* + *p* 7.40 (m,9H)	0.22 0.06	3.90 6H	0.05
10 [Rh(DMAD)(NH$_2$-DAB-CH$_3$)-(PMePh$_2$)$_2$][ClO$_4$]	1.45 (s,6H)	0.52	5.25 (s,4H)	−0.08	*o* 7.50 (m,8H) *m* + *p* 7.39 (m,12H) CH$_3$ 2.08 (s,6H)	0.03 0.02 0.41	3.78 6H	−0.08
11 [Rh(DMAD)(NH$_2$-DAB-CH$_3$)-(PEt$_3$)][PF$_6$]	1.43 (s,6H)	−0.54	5.30 (s,4H)	0.03	CH$_2$ 1.63 (m,6H) CH$_3$ 1.19 (m,9H)	0.24 0.14	3.88 6H	0.02
11' [Rh(DMAD)$_2$(NH$_2$-DAB-CH$_3$)-(PEt$_3$)][PF$_6$]	1.42 (s,3H) 1.23 (s,3H)	−0.55 −0.74	5.29 (s,4H)	−0.04	CH$_2$ 1.60 (m,6H) CH$_3$ 1.00 (m,9H)	0.21 −0.39	3.86 12H 3.80	0.01 −0.05

[a] Chemical shift (δ ppm) from TMS in CDCl$_3$; Δ = δ(complex) − δ(free ligand); [c] obtained at 40 °C (CH$_2$Cl$_2$ reflux).

Table 1a

Elemental analyses for compounds listed in Table 1 ((calc.) found (%))

	C	H	N
1	(56.2)	(4.5)	(2.3)
	55.7	4.1	1.9
1^r	(51.5)	(4.7)	(2.7)
	(51.0	4.2	2.4
2	(59.3)	(5.3)	(2.5)
	58.9	4.9	2.7
2^r	(49.1)	(5.1)	(2.8)
	48.8	4.8	2.7
3	(57.2)	(5.8)	(2.9)
	56.8	6.1	2.6
3^r	(51.6)	(5.5)	(3.1)
	51.8	5.3	3.4
6	(46.5)	(4.3)	(3.2)
	46.2	4.6	3.3
4	(60.1)	(5.4)	(2.7)
	59.9	5.4	3.0
5	(55.1)	(5.7)	(3.1)
	54.9	6.0	3.0
7	(38.8)	(6.1)	(4.1)
	38.6	5.8	3.9
8	(50.6)	(3.7)	(5.1)
	50.9	3.5	5.3
9	(56.2)	(4.7)	(5.7)
	56.4	5.0	5.5
9^r	(46.6)	(4.3)	(7.8)
	46.4	4.5	7.7
10	(50.3)	(4.9)	(6.5)
	50.4	5.1	6.3
11	(30.9)	(5.3)	(9.0)
	31.1	5.5	8.9
11^r	(34.6)	(5.1)	(7.3)
	34.4	5.3	7.5

Reaction of **A** *with DMAD*

A solution of **A** (0.2 mmol) in CH_2Cl_2 (15 ml) was treated with DMAD (0.5 mmol, 0.5 ml) at room temperature or heating under reflux for 3 h; the solution turned red in both cases and immediately H_2 evolution was observed. Concentration of the solution gave a viscous oil, to which ethyl ether was added to induce crystallization. Recrystallization from CH_2Cl_2/CH_3OH/petroleum ether gave orange crystals. Yield 50%.

Spectroscopic data for the products are shown in Table 1, and analyses in Table 1a.

Reactions of **A** *with* $HC{\equiv}CC_6H_5$

The experimental procedure was as described above. When crystallization was induced, long off-white needles were obtained, along with the starting complex.

Table 2

Crystal data, details of data collection (at room temperature) and structure refinement

Crystal data	
Formula	$C_{39}H_{51}N_2O_{13}PClRh$
Crystal habit	orange, transparent, prisms
Crystal size (mm)	$0.15 \times 0.20 \times 0.25$
Symmetry	$2/m$, monoclinic, $P2_1/c$
Unit cell determination	least squares fit from 95 reflections (θ(Cu-K_α) < 43.5°)
Unit cell dimensions (Å)	a 16.720(1), b 12.357(1), c 21.573(1) β 106.53(1)°
Packing: V (Å^3), Z	4273.0(5), 4
D_c (g cm^{-3}), M, $F(000)$	1.44, 925.17, 1920
Experimental data	
Technique	Four circle diffractometer: PW 1100 Philips bisecting geometry Graphite oriented monochromator: Cu-K_α $\omega/2\theta$ scans, scan width: 1.5 Detector apertures 1° × 1°; up θ max 65° 1 min refl.
Number of reflections:	
measured	8002
total independent data	7233
Observed data ($I > 2\sigma(I)$)	6332
Range of hkl	0 18, 0 14, −24 24, (sin θ/λ) max.0.59
Value of R int.	0.047
Standard reflections	2 reflections every 90 min. no variation I
Absorption coefficient	47.77 cm^{-1}
Solution and refinement [14]	
Solution mode	Patterson, Fourier and difference Fourier synthesis
Absorption correction [15]	applied after isotropic refinement
Refinement mode	least squares or F's,observed reflections only, anisotropic for non hydrogen and isotropic for fixed H atoms
Parameters:	
Number of variables	514
Degrees of freedom	5818
Ratio of freedom	11.3
H-atoms	difference synthesis
Final shift/error	0.04 average
w-scheme [16]	empirical so as to give no trends in $\langle w\Delta^2F \rangle$ vs. $\langle F_0 \rangle$ and $\langle \sin\theta/\lambda \rangle$
Max. thermal value	$U_{22}(O_{13}) = 0.276$
ΔF final	1.58 e Å^{-3} near Rh atom
Extinction correction	no correction applied
S	1.95
R, R_w	0.062, 0.045
Computer and programs	VAX 11/750, XRAY80 [14], DIFABS [15], PESOS [16], PARST [17]
Atomic factors	neutral atoms and anomalous dispersion factors from International tables from ref. 18

X-Ray analysis of $[\overline{RhC(CO_2Me)=C(CO_2Me)C(CO_2Me)=C}CO_2Me(c\text{-}Hex\text{-}DAB)\text{-}(PMePh)_2H_2O]ClO_4$

The crystals were coated with paraffin oil and sealed in a Lindeman glass capillary tube. Crystal data and details of the processing procedure are given in Table 2. 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 Walker and Stuart's method [15], and the structure was refined by full matrix least squares methods with anisotropic thermal parameters. The H atoms were located from successive difference maps and were included in the refinement with isotropic thermal parameters of the atoms to which they are attached. Agreement factors are defined as $R = \Sigma|\Delta|/\Sigma|F_o|$ and $R_w = (\Sigma w^2/\Sigma w|F_o|^2)^{1/2}$, $(\Delta = |F_o| - |F_c|)$.

A table of thermal parameters and lists of observed and calculated structure factors are available from the authors.

Results and discussion

(a) Reactions of A with DMAD

The rhodium *cis*-dihydrides **A** react readily with an excess of DMAD in CH_2Cl_2 at room temperature with evolution of hydrogen usually to give compounds of stoichiometry $[Rh(DMAD)(R\text{-}DAB)(PR'_3)_2]^+$ with a 1/2 DMAD/PR'_3 ratio; see Scheme 1 (compounds **1**, **2**, **4**, **5**, **8**, **9**, **10**) and Scheme 2 (compound **B**). The loss of one phosphine in the case of products **6**, **7**, **11**, may be due to steric factors. For $PR_3 = PMePh_2$, compound **3**, with a 2/2 DMAD/$PMePh_2$ ratio, is obtained.

When the reactions are carried out at 40 °C (CH_2Cl_2 reflux), phosphine is eliminated and two molecules of DMAD are incorporated; these are dimerized and form a metallacyclopentadiene complex (Scheme 2, C) with a 2/1 DMAD/PR_3 ratio; this is the case with compounds, **1**^{r}, **2**^{r}, **3**^{r}, **8**^{r}, **10**^{r}, in Table 1. The determination of the structure of compound **3**^{r} confirmed the formation of an intermediate species in the cyclotrimerization of alkynes; a redistribution of ligands has also been observed, as can be seen for complex **D** in Scheme 2.

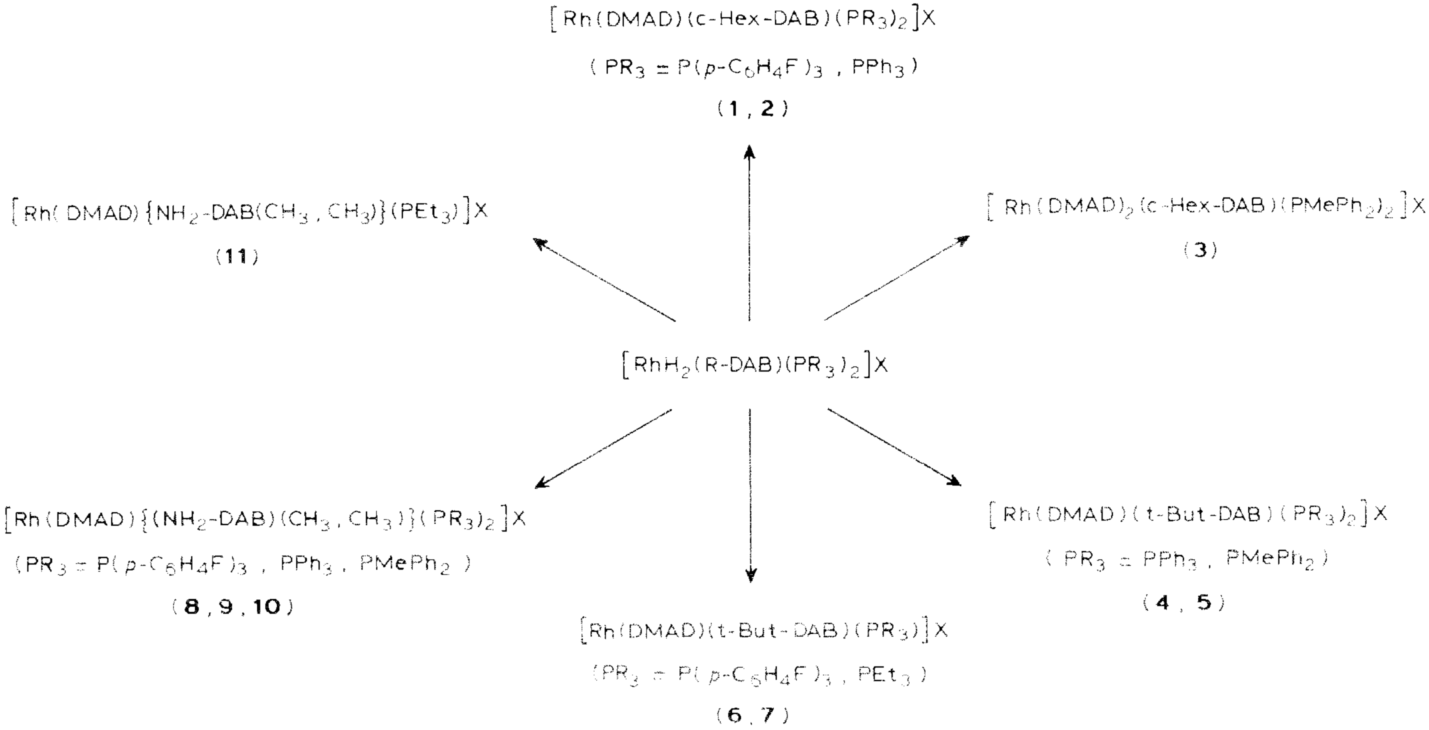
For $PR'_3 = PEt_3$ and RDAB = c-Hex-DAB, there is no reaction at room temperature, and under reflux decomposition occurs.

The compounds obtained are air stable and behave as 1/1 electrolytes.

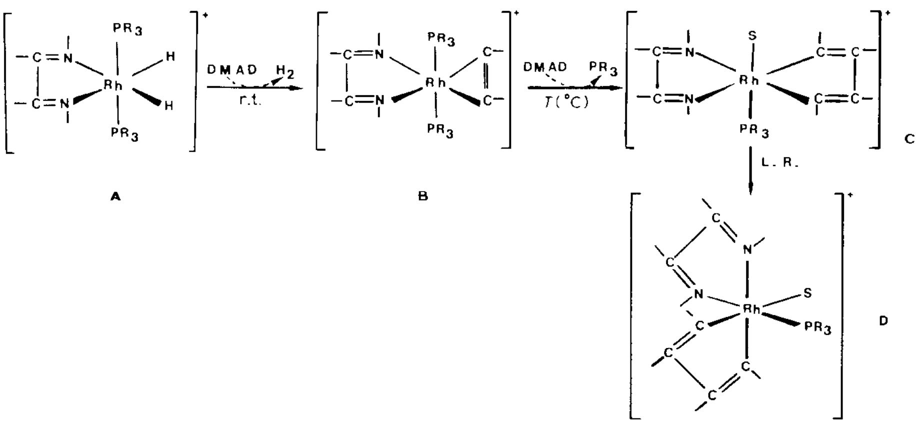
Spectroscopic characterization

The main infrared vibrations (cm^{-1}) observed for the $[Rh(DMAD)_n(R\text{-}DAB)(PR_3)_m]^+$ (n, m = 1, 2) in KBr disks are: weak bands at 2980–2960 cm^{-1} attributed to $\nu(C\text{-}H)_{DMAD}$; 1730–1710 cm^{-1}, a structured strong broad absorption band due to $\nu(C{=}O)_{DMAD}$ and $\delta(C\text{-}H)_{DMAD}$ at 1270–1250. The $\nu(C{=}C)$ and $\nu(C{=}N)$ bands are observed at 1620 cm^{-1} with weak to medium intensity. The perchlorate anion gives a $\nu(Cl\text{-}O)$ band at 1090 cm^{-1} and a $\nu(OClO)$ band at 610 cm^{-1}. No products derived from insertion of the alkyne into the Rh–H bond were detected.

^1H NMR data are summarized in Table 1. The integrated ^1H resonances confirm the presence of 1 or 2 phosphine, 1 R-DAB, and 1 or 2 acetylene molecules in every complex, in agreement in each case with the elemental analysis. The compounds



Scheme 1. Compounds formed in the reactions of rhodium dihydrides with DMAD at room temperature.



Scheme 2. r.t. = room temperature; $T = 40\,°\mathrm{C}$ (CH_2Cl_2 reflux); L.R. = ligand redistribution.

have been grouped together for each R-DAB ligand in the basis of the basicity of the phosphine; those shown with the superscript "*r*" were obtained at 40 °C (CH_2Cl_2 reflux).

When R-DAB ligands are coordinated to rhodium σ-N(1), σ-N(2), imine protons give only one signal (Table 1); the appearance of two signals would raise the possibility of asymmetric coordination.

In view of the structure of compound 3^r, **B**, we suggest that the interaction between an iminic carbon and an oxygen of the perchlorate is responsible for the double signal from this compound in solution. The cyclohexyl resonances appear in the range δ 0.5–2.85 with a resolution that allowed us to distinguish between axial and equatorial protons. The column of Δ values, the difference between δ(complex) and δ(free ligand), shows that resonances shift upfield on complexation. They were expected to shift downfield, but the presence of aromatic rings in the phosphine coordinated to rhodium leads to aromatic ring current effects that are apparent in the δ-values of nearby protons and are superimposed on the downfield effect above mentioned.

For DMAD there is essentially no shift of the methyl ^1H resonances upon coordination [19]: δ 3.86 ppm for the free ligand and δ 3.52–3.90 ppm for the complex in $CDCl_3$. The compounds with two molecules of DMAD show a significant shift upfield.

Crystal structure of $[\overline{RhC(CO_2CH_3)=C(CO_2CH_3)C(CO_2CH_3)=C}(CO_2CH_3)(C_6H_{11}N{=}CHCH{=}NC_6H_{11})\{PCH_3(C_6H_5)_2\}H_2O]ClO_4$ ***(B)***

The molecular structure of the cation of **B** is illustrated in Fig. 1, with non-hydrogen atoms numbered. Atomic positional parameters and relevant bond length and bond angle data are given in Tables 3 and 4.

The inner coordination sphere can be considered to be a distorted octahedron with the ligands distributed around the rhodium as shown in Fig. 2. The c-Hex-DAB ligand is σ-N(1), σ-N(2) coordinated, with the skeleton N=CC=N practically planar; deviations from this least-squares plane are < 0.008 Å; the rhodium atom deviates from this plane by 0.05 Å; cyclohexyl rings on both imine N atoms are in the chair

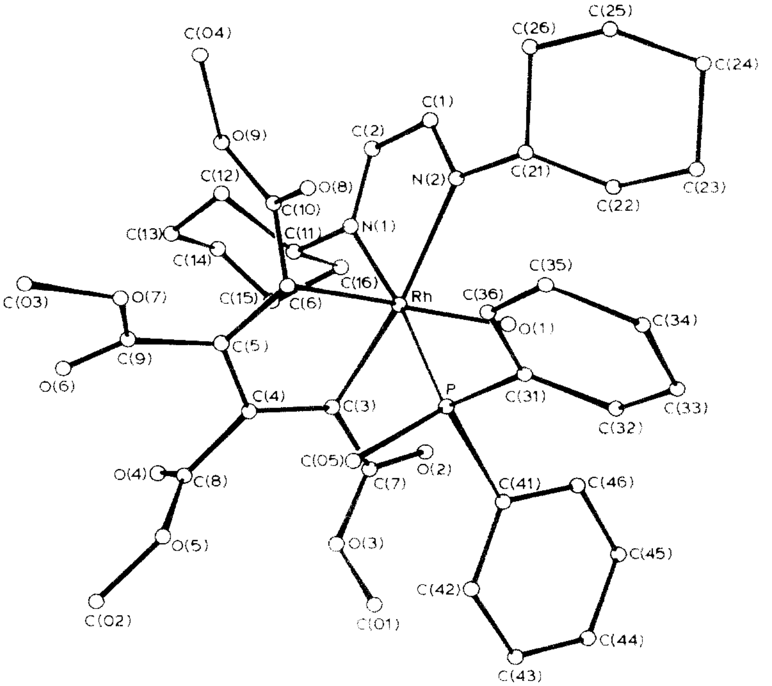


Fig. 1. Molecular structure of the cation $[\mathrm{Rh\overline{C(CO_2CH_3)=C(CO_2CH_3)C(CO_2CH_3)=C}(CO_2CH_3)}]^+$ in complex **B**.

conformation with an average C–C distance of 1.517(6) Å and an average C–C–C angle of 111.4(4)°. One of the rings shows high thermal vibration. The angle between the least-squres plane of the planar part of the cyclohexyl ring and the plane N=CC=N is 88°. The distances Rh–N(1) and Rh–N(2) are 2.107(5), 2.179(4) Å. The angle N(1)RhN(2) is 76.7(2)° and N(1)=C(2), N(2)=C(1) distances are 1.267(9), 1.281(8) Å. If the C=N distances in free and coordinated c-Hex-DAB are compared it can be seen that they lengthen on coordination; a comparison of these distances with those for coordinated ph-DAB, in complex $[\mathrm{RhH_2(ph\text{-}DAB)(PPh_3)_2}]^+$ [13], 1.277(16) and 1.275(19) Å, reveals a longer C=N distance arising from the better π-acceptor capability of ph-DAB. The same effect is seen for the distances Rh–N(1), Rh–N(2), and the angle N(1)RhN(2).

In the metallocyclic pentadiene ring formed by C(3)C(4)C(5)C(6)Rh the four carbon atoms form a plane with the rhodium atom at 0.12 Å out of this plane. The bond lengths C(6)=C(5) and C(3)=C(4) are 1.349(8) and 1.362(8) Å and are longer than the C=C bonds in free butadiene, 1.341 Å. The angle C(3)RhC(6) is 80.3(2)°. The least squares plane C(3)C(4)C(5)C(6) makes an angle of 98.7(3)° with the planar skeleton of c-Hex-DAB; other relevant least squares planes in the molecule are those formed by the atoms N(1)N(2)PC(3) and C(6)C(3)N(2)O(1).

The Rh–P distance is 2.361(2) Å, and the two phenyl rings of the phosphine ligand make an angle of 105.2(2)°.

A molecule of water taken up during crystallization completes the 6-coordination at rhodium. It is important to note that one of the two hydrogen atoms, H(11) is

Table 3. Atomic parameters for complex **3'**, with thermal parameters as $U_{eq} = \frac{1}{3}\Sigma(U_{ij} \cdot a_i^\star \cdot a_j^\star \cdot a_i \cdot a_j \cdot \cos(a_i,a_j) \times 10^4)$

Atom	x	y	z	U_{eq}
Rh	0.24226(3)	0.16731(4)	0.39337(2)	412(1)
Cl	0.6296(1)	0.1222(1)	0.4245(1)	663(7)
P	0.1495(1)	0.3026(1)	0.4079(1)	459(5)
O(1)	0.2252(2)	0.0629(3)	0.4709(2)	564(16)
O(2)	0.0919(3)	−0.0189(4)	0.3830(2)	655(18)
O(3)	0.0022(2)	0.0552(3)	0.2989(2)	522(15)
O(4)	0.0661(3)	0.0326(3)	0.1786(2)	607(17)
O(5)	0.0165(3)	0.2000(3)	0.1824(2)	612(16)
O(6)	0.1741(3)	0.2401(4)	0.1467(2)	803(21)
O(7)	0.2404(3)	0.3727(3)	0.2084(2)	570(16)
O(8)	0.3438(3)	0.4027(4)	0.3534(2)	766(21)
O(9)	0.3869(4)	0.2692(4)	0.2999(2)	643(18)
O(10)	0.7135(3)	0.1279(5)	0.4253(3)	1176(32)
O(11)	0.5988(4)	0.2218(5)	0.4372(4)	1501(43)
O(12)	0.6213(4)	0.0473(6)	0.4689(4)	1509(40)
O(13)	0.5803(5)	0.0857(8)	0.3647(3)	1871(50)
N(1)	0.3197(3)	0.0464(4)	0.3726(2)	541(19)
N(2)	0.3646(3)	0.2057(4)	0.4585(2)	517(18)
C(1)	0.4202(4)	0.1412(6)	0.4513(3)	617(26)
C(2)	0.3971(4)	0.0552(6)	0.4036(3)	624(26)
C(3)	0.1390(3)	0.1169(4)	0.3242(3)	407(19)
C(4)	0.1352(3)	0.1516(4)	0.2635(2)	400(18)
C(5)	0.2021(3)	0.2279(4)	0.2603(3)	420(20)
C(6)	0.2578(3)	0.2465(5)	0.3182(3)	458(20)
C(7)	0.0781(3)	0.0437(5)	0.3388(3)	455(21)
C(8)	0.0703(3)	0.1184(5)	0.2035(3)	460(21)
C(9)	0.2028(3)	0.2774(5)	0.1993(3)	450(21)
C(10)	0.3340(4)	0.3153(6)	0.3256(3)	532(33)
C(01)	−0.0620(4)	−0.0072(6)	0.3140(3)	610(26)
C(02)	−0.0490(4)	0.1828(7)	0.1225(4)	890(33)
C(03)	0.2508(4)	0.4313(6)	0.1532(3)	733(31)
C(04)	0.4614(4)	0.3311(7)	0.3025(4)	952(38)
C(05)	0.1028(4)	0.3794(5)	0.3355(3)	563(23)
C(11)	0.2938(4)	−0.0403(6)	0.3221(3)	680(27)
C(12)	0.3516(6)	−0.0539(9)	0.2807(4)	1280(54)
C(13)	0.3134(7)	−0.1405(9)	0.2301(5)	1379(60)
C(14)	0.2984(8)	−0.2448(9)	0.2575(6)	1487(66)
C(15)	0.2471(9)	−0.2303(9)	0.3006(7)	1843(88)
C(16)	0.2823(7)	−0.1439(7)	0.3544(5)	1345(57)
C(21)	0.3856(4)	0.2884(5)	0.5095(3)	565(23)
C(22)	0.3586(4)	0.2518(6)	0.5668(3)	727(29)
C(23)	0.3727(5)	0.3377(7)	0.6189(3)	907(36)
C(24)	0.4635(5)	0.3732(8)	0.6397(4)	959(38)
C(25)	0.4880(5)	0.4125(7)	0.5826(4)	1012(41)
C(26)	0.4775(4)	0.3221(7)	0.5305(3)	826(32)
C(31)	0.1845(4)	0.4143(5)	0.4640(3)	504(22)
C(32)	0.1551(5)	0.4307(6)	0.5176(3)	714(30)
C(33)	0.1775(5)	0.5222(7)	0.5553(4)	886(37)
C(34)	0.2311(5)	0.5982(6)	0.5407(4)	844(36)
C(35)	0.2616(4)	0.5828(5)	0.4877(4)	703(29)
C(36)	0.2377(4)	0.4905(5)	0.4501(3)	623(26)
C(41)	0.0610(4)	0.2468(5)	0.4299(3)	487(21)
C(42)	−0.0200(4)	0.2621(5)	0.3915(3)	623(26)
C(43)	−0.0856(4)	0.2186(7)	0.4110(4)	783(32)
C(44)	−0.0727(4)	0.1597(7)	0.4678(4)	768(32)
C(45)	0.0077(5)	0.1447(6)	0.5054(3)	658(28)
C(46)	0.0734(4)	0.1868(5)	0.4877(3)	553(23)

Table 4

Selected bond distances and angles for complex **3**′

Bond distances (Å)			
Rh–P	2.361(2)	Rh–O(1)	2.194(4)
Rh–C(3)	2.032(5)	Rh–C(6)	1.974(7)
Rh–N(1)	2.107(5)	Rh–N(2)	2.179(4)
N(1)–C(2)	1.281(8)	N(2)–C(1)	1.267(9)
N(1)–C(11)	1.501(8)	N(2)–C(21)	1.469(8)
C(1)–C(2)	1.454(10)	C(3)–C(4)	1.362(8)
C(3)–C(7)	1.462(8)	C(4)–C(8)	1.491(7)
C(4)–C(5)	1.480(7)	C(5)–C(6)	1.349(8)
C(5)–C(9)	1.454(9)	C(6)–C(10)	1.502(8)
C(7)–O(2)	1.198(8)	C(7)–O(3)	1.323(6)
C(3)–O(4)	1.182(7)	C(8)–O(5)	1.342(7)
C(9)–O(7)	1.323(7)	C(9)–O(6)	1.192(7)
C(10)–O(9)	1.301(9)	C(01)–O(3)	1.432(8)
C(02)–O(5)	1.452(8)	C(03)–O(7)	1.446(8)
C(04)–O(9)	1.449(9)		
Bond angles (°)			
P–Rh–C(6)	90.2(2)	O(1)–Rh–N(1)	88.1(2)
O(1)–Rh–N(2)	86.5(2)	O(1)–Rh–C(3)	96.4(2)
O(1)–Rh–C(6)	173.7(2)	N(1)–Rh–N(2)	76.7(2)
N(1)–Rh–C(3)	94.1(2)	N(1)–Rh–C(6)	86.8(2)
N(2)–Rh–C(3)	170.3(2)	N(2)–Rh–C(6)	95.9(2)
C(3)–Rh–C(6)	80.3(2)	C(3)–C(4)–C(5)	114.6(4)
C(4)–C(5)–C(6)	113.4(5)	Rh–C(3)–C(4)	114.0(4)
Rh–C(6)–C(5)	117.3(4)	Rh–N(1)–C(2)	114.8(4)
Rh–N(2)–C(1)	111.8(5)		
Torsion angles (°)			
C(46)–C(41)–P–C(31)	−72.5(6)	C(05)–P–C(41)–C(46)	−175.7(5)
O(1)–Rh–N(2)–C(21)	−85.0(5)	C(22)–C(21)–N(2)–Rh	74.9(6)
C(10)–C(6)–Rh–C(3)	−177.9(5)	Rh–C(3)–C(4)–C(5)	−5.8(6)
C(3)–C(7)–O(3)–C(01)	−174.6(5)		

near O(12) of the perchlorate anion, giving an intermolecular contact of 1.675(6) Å, and the other hydrogen, H(12), is near O(2) of a carbonyl group, giving an intramolecular contact of 1.937(4) Å. The perchlorate oxygens show short contacts

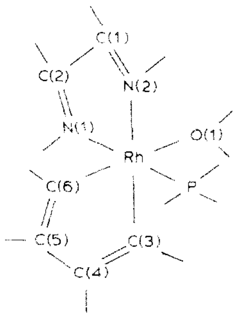


Fig. 2. Ligand distribution around the rhodium in complex **B**.

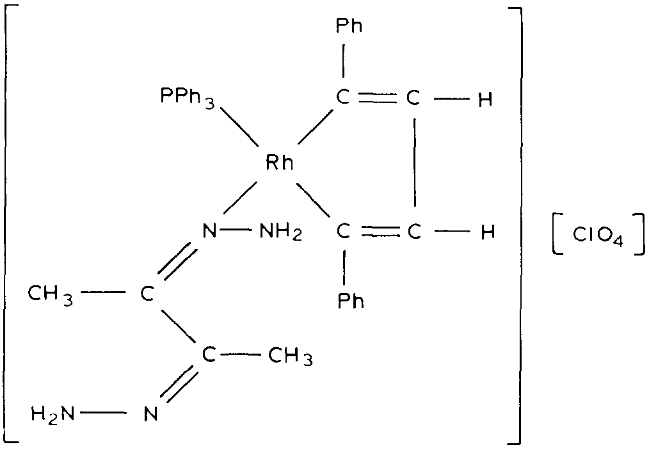
with some carbon atoms of the complex cation: the most remarkable is the C(1)–O(12) distance of 3.090(12) Å, which we suggest is responsible for the double signal from the imine proton in the ^1H NMR spectrum even of solutions.

(b) Reactions of $[RhH_2(R\text{-}DAB)(PR_3)_2]$ with HC≡CPh

We extended the study to reactions with the non-activated alkyne HC≡CPh. The reactions are rapid and take place with hydrogen evolution. In all cases unchanged starting hydride was revealed along with off-white needles of composition $C_{24}H_{18}(HC{\equiv}CPh)_3$; they were characterized by elemental analysis, mass spectrometry, and ^1H NMR spectroscopy. Their ^1H NMR spectra show two multiplets at 6.96 (*ortho*, 6H) and 6.63 ppm (*meta* + *para*, 9H), and a singlet (3H) at 5.85 ppm.

An intermediate species in the cyclotrimerization of $CH{\equiv}CC_6H_5$ has been isolated for $NH_2N{=}CCH_3CCH_3{=}NNH_2$ and $P(C_6H_5)_3$; this complex, of composition $[Rh(NH_2\text{-}DAB,CH_3)(HC{\equiv}CPh)_2(PPh_3)][ClO_4]$, shows the following resonances in its ^1H NMR spectrum: two signals at 7.43 and 7.29 ppm from the aromatic protons of the phosphine and HC≡CPh ligands; a singlet at 5.93 ppm from the HC= protons, a singlet at 5.04 ppm signal from the NH_2 protons and two singlets at 1.43 and 1.24 ppm from the methyl-imine group. The fact that the two methyl imine groups have different chemical shifts may be an indication that the DAB ligand is joined asymmetrically to the metal owing to the steric effect of the CH_3 groups. The tendency of this ligand to behave as monodentate has been noted previously [20].

The integrated ^1H resonances and the elemental analysis for C, H, N (% found/calc. 58.08 (58.3), 4.9 (4.7), 7.0 (7.2)) support the stoichiometry proposed above. A possible structure in agreement with these results is shown below:



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1 R-DAB, RN=CHCH=NR; R = cyclohexyl or t-Bu, R-DABR′, RN=CR′CR′=NR; R = NH_2, R′ = CH_3. PR'_3 = P(*p*-$C_6H_4F)_3$, PPh_3, $PMePh_2$, or PEt_3. Nomenclature according to G. van Koten and K. Vrieze, Adv. Organomet. Chem., 21 (1982) 151.

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