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Reactions of the hexaaquarhodium(III) cation with bis(benzimidazol-2-ylmethyl)methylamine and PPh_3: syntheses and properties of new hydrido- and carbonylrhodium complexes

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Abstract

Hexaaquarhodium(III) perchlorate has been found to be an interesting starting material for the preparation of rhodium compounds. New mononuclear hydrido- and carbonylrhodium compounds with bis(benzimidazol-2-ylmethyl)methylamine (L) and PPh_3 of the type $[Rh(H)L(PPh_3)_2](ClO_4)_2$ (**1**) and $[Rh(CO)L(PPh_3)_2](ClO_4)$ (**2**) have been synthesized. The monomeric Rh(II) compound was identified as an intermediate. Complexes **1** and **2** were characterized by elemental analysis, mass spectrometry and IR, and NMR spectroscopies. The fluxional behaviour of **2** was studied by variable-temperature ^1H and $^{31}P\{H\}$ NMR experiments.

Keywords: Rhodium complexes; Aqua complexes; Benzimidazolato complexes; Hydrides; Carbonyls

1. Introduction

The versatile behaviour of transition metal chelates of N-donor ligands is the subject of ongoing research. Many chemists have incorporated imidazole groups in stable chelates to obtain ligand systems [1,2]. A certain flexibility of the ligand, whereby the coordination geometries may adapt to oxidation state changes and to one or two ''open'' positions at the metal ion site [3], may facilitate catalytic reactions. Synthesis of metal complexes of bridged bis(benzimidazole) ligands of various bridge type donor groups is of great interest for their physiological activity and interesting stereochemistry.

Complexes of bridged bis(imidazole) and bis(benzimidazole) ligands of various bridge types with transition metals were examined as potential models of the structure and mobility of biological metal binding sites in metalloproteins. One of these is bis(benzimidazol-2-ylmethyl)methylamine (L) (Fig. 1).

Interest in the chemistry of rhodium compounds stems from their activity in many homogeneous catalytic processes, such as hydrogenation [4], hydroformylation [4d,5] decarbonylation [4e], carbonylation [5e,6], hydrosililation [7], reductive amination [8], oxidation [9–12], cyclopropanation and cycloaddition [13]. Rhodium compounds show interesting antitumour activity and represent the most promising candidates for the development of structurally related platinum analogues [14]. Antibacterial action of some rhodium complexes in structures of the type $[RhCl_2(py)_4]Cl$, $[Rh_2X_2(RCOO)_2(N\text{-}N)_2]$ and $[Rh_2(RCOO)_2(N\text{-}N)_2(H_2O)_2]^{2+}$ (X = Cl, Br, I; R = H, Me, PhCHOH; N-N = 2,2′-bipyridine, 1,10-phenantroline and their derivatives) has also been demonstrated [15].

Numerous publications have appeared regarding metals like Cu [16–19], Zn, Pd, Pt [19], Fe [1,2,20,21] Mn [1,2,22], Co [19,23], Ni [19,24], Ru [25], but only a few reports are available on rhodium compounds with the ligand in question [26–28]. There is no data on this type of compound containing simultaneously coordinated

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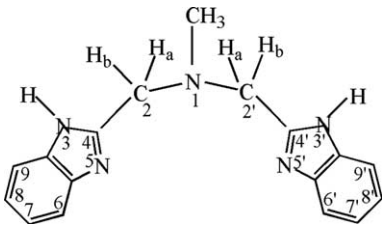


Fig. 1. Bis(benzimidazol-2-ylmethyl)methylamine (**L**).

hydride anions or carbonyl ligands. It has been demonstrated that different rhodium(III) substrates, like $RhCl_3 \cdot 3H_2O$ and $[R(H_2O)_6](ClO_4)_3$, used as the reagents for syntheses of rhodium compounds, affect the stoichiometry of the substitution products [27,28, 29a,29b].

As a continuation of the research performed in this laboratory over the past several years, aimed to investigate the chemistry of homoleptic aqua rhodium complexes [27–29], we have examined the reactivity of $[Rh(H_2O)_6](ClO_4)_3$ in substitution reaction with bis(benzimidazol-2-ylmethyl)methylamine and PPh_3. Here, we report on the preparation and characterization of the title complexes.

2. Experimental

2.1. Materials and physical measurements

$RhCl_3 \cdot 3H_2O$ was purchased from Pressure Chemical Co. All other chemicals were reagent grade and were used as commercially available. Infrared spectra were recorded on a FT-IR Nicolet Impact 400 spectrometer in the 4000–400 cm^{-1} range as KBr disks or Nujol mulls. The NMR spectra were collected on a Bruker AMX-300 spectrometer (^1H at 300.13 MHz, ^{31}P at 121.496 MHz) and on a Bruker Avance–500 spectrometer (^1H at 500.13 MHz, ^{13}C at 125.76 MHz) with TMS as internal standard for ^1H and $^{13}C\{H\}$, and 85% H_3PO_4 as external standard for $^{31}P\{H\}$. ESR spectra were monitored for solutions and solids on a Bruker ESP 300E spectrometer. Elemental analyses were performed at the Elemental Analysis Centre of Wrocław University on a Perkin–Elmer Elemental Analyser 2400 for CHN. Mass spectra were measured on a Finnigan Mat. TSQ 700. Catalytic reaction products were analysed on a GS-MS Hewlett–Packard instrument: HP 5890 II chromatograph with HP 5971a mass detector. Bis(benzimidazol-2-ylmethyl)methylamine (**L**) was synthesized as described [27,28]. $[Rh(H_2O)_6](ClO_4)_3$ was prepared according to the method of Ayres and Forrester [30] in the reaction of $RhCl_3 \cdot 3H_2O$ with concentrated perchloric acid and standardized spectrophotometrically using the known UV–Vis spectrum of $[Rh(H_2O)_6](ClO_4)_3$ with peaks at 396 nm ($\varepsilon = 62$ M^{-1} cm^{-1}) and 316 nm ($\varepsilon = 67.4$ M^{-1} cm^{-1}) as described by Reynolds and coworkers [31].

2.2. Syntheses of the complexes

2.2.1. $RhL(H)(PPh_3)_2](ClO_4)_2$ (**1**)

(**a**) To a 1–3 M $HClO_4$/EtOH solution of $[Rh(H_2O)_6](ClO_4)_3$ (0.273 mmol, 4 cm^3) heated to 348 K under a nitrogen atmosphere was slowly added deoxygenated L (0.273 mmol, 79 mg) in 10 cm^3 of EtOH and next a deoxygenated solution of PPh_3 (0.819 mmol, 215 mg) in 10 cm^3 EtOH. The resulting red mixture was stirred under an inert atmosphere at 348 K for 5 h, next oxygenated with O_2 until the colour changed to yellow, and further stirred at room temperature for 20 h under N_2. The deposited greyish-white precipitate was filtered off and washed with deaerated EtOH and Et_2O. The crude product was dissolved in acetone and EtOH (1:1). Careful evaporation under a slow flow of nitrogen afforded white precipitate of **1**. It was filtered off and vacuum dried.

Yield: 214 mg (70%). Found: C, 56.75; H, 4.22; N, 6.18; Cl, 5.56%. $C_{53}H_{48}N_5P_2O_8Cl_2Rh$ ($M = 1118.72$) requires: C, 56.90; H, 4.33; N, 6.26; Cl, 5.54%. Positive-ion ESI-MS ($CHCl_3$) m/z 1018.7 [{RhL(H)$(PPh_3)_2$}(ClO_4)]$^+$; 919.9 $[RhL(H)(PPh_3)_2]^{2+}$. Selected IR absorption bands (KBr, cm^{-1}): 1624 m, 1480 s, 1437 s, 1185 sh, 1092 vs, br, 746 s, 699 s, 624 s, 520 s; (nujol) 2180 m ν(Rh–H). NMR spectra, δ (ppm), ^1H (acetone-d_6): −14.4 (dt, 1H $J_{P,H} = 18.4$, $J_{Rh,H} = 25.1$ Hz); 3.36 (s, 3H, N_1–CH_3); 3.49, 4.35 (dd, 4H, $2H_a$, $2H_b$, $J_{ab} = 17.5$ Hz); 7.05–7.32 (m, 8H $H^{6,6'}$, $H^{7,7'}$, $H^{8,8'}$, $H^{9,9'}$ + 30 H $P(C_6H_5)_3$); 12.1 (s, 2H, $N^{3,3'}$–H); $^{31}P\{H\}$: 35.17 (d, $J_{Rh,P} = 116.8$ Hz); (CD_2Cl_2): −14.74 (dt, 1H, $J_{P,H} = 18.0$ Hz); 2.93 (s, 3H, N_1–CH_3); 2.87, 3.95 (dd, 4H, $2H_a$, $2H_b$, $J_{ab} = 17.6$ Hz); 6.92–7.65 (m, 38 H aryl H); 12.24 (s, 2H, $N^{3,3'}$–H); $^{31}P\{H\}$: 35.1 (d, $J_{Rh,P} = 116.9$ Hz).

(**b**) The above procedure was applied to the reaction carried out in MeOH. A greyish-white solid was precipitated and was filtered off, washed with MeOH and Et_2O, and dried in vacuo. Yield: 183 mg (60%). Found: C, 56.50 5; H, 4.52; N, 6.20; Cl, 5.46%. $C_{53}H_{48}N_5P_2O_8Cl_2Rh$ ($M = 1118.72$) requires: C, 56.90; H, 4.33; N, 6.26; Cl, 5.54%. Positive-ion ESI-MS ($CHCl_3$) m/z 1018.7 [{RhL(H)$(PPh_3)_2$}(ClO_4)]$^+$; 919.9 $[RhL(H)(PPh_3)_2]^{2+}$. Selected IR absorption bands (Nujol, cm^{-1}): 2176 m ν(Rh–H), 1624 m, 1076 br s,749 s, 696 s, 612 s, 523 s. NMR spectra (CD_3CN), δ (ppm), ^1H: −14.43 (dt, 1H $J_{P,H} = 17.4$, $J_{Rh,H} = 24.8$ Hz); 3.24 (s, 3H, N_1–CH_3); 3.38, 4.22 (dd, 4H $2H_a$, $2H_b$, $J_{ab} = 17.5$ Hz)); 6.94–7.43 (m, 38H aryl H), 12.1 (s, 2H, $N^{3,3'}$–H); $^{31}P\{H\}$: 35.3 (d, $^1J_{Rh,P}$) = 117.1 Hz).

2.2.2. $RhL(CO)(PPh_3)_2](ClO_4)$ (**2**)

To a 1–3 M $HClO_4$/EtOH solution of $[Rh(H_2O)_6](ClO_4)_3$ (0.273 mmol, 4 cm^3) heated to 348 K under an argon atmosphere was slowly added deoxygenated L (0.273 mmol, 79 mg) in 10 cm^3 EtOH and

next a deaerated solution of PPh_3 (0.819 mmol, 215 mg) in 10 cm^3 EtOH. The resulting red mixture was stirred under argon at 348 K for 5 h and next for 20 h at room temperature. A deposited pale-yellow solid was filtered and washed with degassed EtOH and Et_2O. The crude product was dissolved in a mixture of CH_2Cl_2, $CHCl_3$ and EtOH (1:1:1) and gently evaporated under a nitrogen flow. The pale yellow micro-crystals were collected by filtration, washed with cold ethanol, and vacuum dried. Yield: 171 mg (60%). Found: C, 60.98; H, 4.46; N, 6.45%. $C_{54}H_{47}N_5P_2O_5Cl_1Rh_1$ ($M = 1046.29$ requires: C, 61.99; H, 4.53; N, 6.69%. Positive-ion ESI-MS ($CHCl_3$) m/z 946.6 $[RhL(CO)(PPh_3)_2]^+$. Selected IR absorption bands (KBr, cm^{-1}): 2002 vs, 1481 m, 1458 m, 1436 s, 1115 sh, 1094 br vs, 746 s, 698 s, 623 m, 521 s; (Nujol) 2006 s. NMR spectra ($CDCl_3$), δ (ppm), ^1H: 0.36 (s, 3H, N_1–CH_3), 2.66 and 3.98 (dd, 4H, $2H_a$, $2H_b$, $J_{ab} = 17.2$ Hz), 7.69–6.74 (m, 8H, $H^{6,6'}$, $H^{7,7'}$, $H^{8,8'}$, $H^{9,9'}$ + 30H $P(C_6H_5)_3$), 11.23 (s, 2H, $N^{3,3'}$–H); $^{31}P\{H\}$: 29.46 (dd, $^1J_{Rh,P} = 128.8$ Hz, $J_{P,P} = 28.9$Hz); (CD_2Cl_2): 0.47 (s, 3H, N_1–CH_3), 4.0–3.5 (s br, 4H, 4 $H_{a,b}$), 7.6–6.78 (m, 38 H aryl H), 11.34 (s, 2H, $N^{3,3'}$–H); $^{31}P\{H\}$: 29.25 (d, $^1J_{Rh,P} = 128.8$ Hz); (acetone-d_6): ^1H: 0.57 (s, 3H, N_1–CH_3), 3.42–3.38 (m, 4H, $4H_{a,b}$), 8.0–6.83 (m, 38H aryl H), 11.56 (s, 2H, $N^{3,3'}$–H); $^{31}P\{H\}$: 30. 57 (d, $^1J_{Rh,P} = 128.1$ Hz). $^{13}C\{H\}$: 189.1 (dt, $^1J_{Rh,C} = 68.3$ Hz, $^2J_{CRhP} = 17.2$ Hz).

Catalytic runs. To a 1–3 M $HClO_4$/ROH (R = Me, Et) solution of $[Rh(H_2O)_6](ClO_4)_3$ (0.225 mmol) heated to 348 K under a nitrogen atmosphere was slowly added deoxygenated L (0.225 mmol) in 10 cm^3 of ROH and next a deoxygenated solution of PPh_3 (0.675 mmol) in 10 cm^3 ROH. The unsaturated substrate like 1-hexene or cyclohexene (2.25 mmol) was added subsequently. The resulting mixture was stirred under an inert atmosphere at 348 K for 3 h. Organic products were analysed with GC–MS after separation from the rhodium complexes by vaccum transfer.

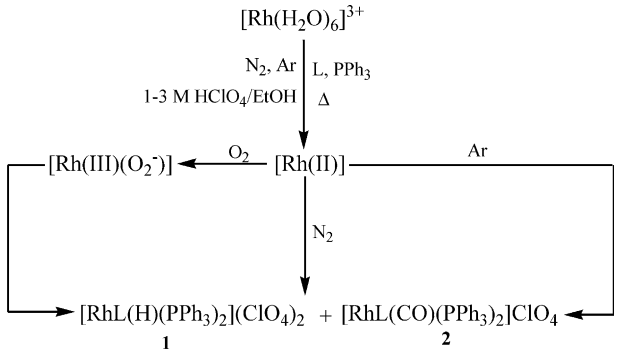
Caution. Although no accident occurred with the rhodium perchlorate complexes during the experimental work, it should be remembered that perchlorates are potentially explosive. They should be prepared in small quantities and handled with care.

3. Results and discussion

3.1. Synthesis, ESR and IR characterization

The preparations and principal reactions of complexes described in this paper are presented in Scheme 1.

Hexaaquarhodium(III) perchlorate in acidic water ethanolic solution has been found to react with L giving complexes $[RhL(H_2O)_2(ClO_4)](ClO_4)_2$ and $[RhL_2](ClO_4)_3 \cdot 3H_2O$ for 1:1 and 1:2 metal-to-ligand molar ratios, respectively [27,28].



L = bis(benzimidazol-2-ylmethyl)methylamine

Scheme 1.

Dropwise addition of ethanolic solution containing L to a solution of $[Rh(H_2O)_6]^{3+}$ in 1–3 M $HClO_4$/EtOH, warmed up to 348 K, leads to a colour change from yellow to yellow-brown. Subsequent addition of PPh_3 in EtOH causes a discernible darkening to dark red after several minutes for reactions carried out both under an N_2 and Ar atmosphere.

The ESR spectrum of the resulting mixture in liquid nitrogen exhibits near axial symmetry with $g_{xx,yy} = 2.29$, $g_{zz} = 1.99$ ($g_{av} = 2.19$) (Fig. 2(a)), comparable with those published for other monomeric rhodium(II) compounds [32].

This indicates that the reduction of Rh(III) to Rh(II) takes place during the first reaction steps, reaction (1).

$$[Rh^{III}(H_2O)_6]^{3+} + L + PPh_3 \xrightarrow[\Delta\ N_2(Ar)]{H^+/H_2O/EtOH} [Rh^{II}L(PPh_3)_2]^{2+} \quad (1)$$

The stoichiometry of the final products suggests that the Rh(II) species is a monomeric $[RhL(PPh_3)_2]^{2+}$ cat-

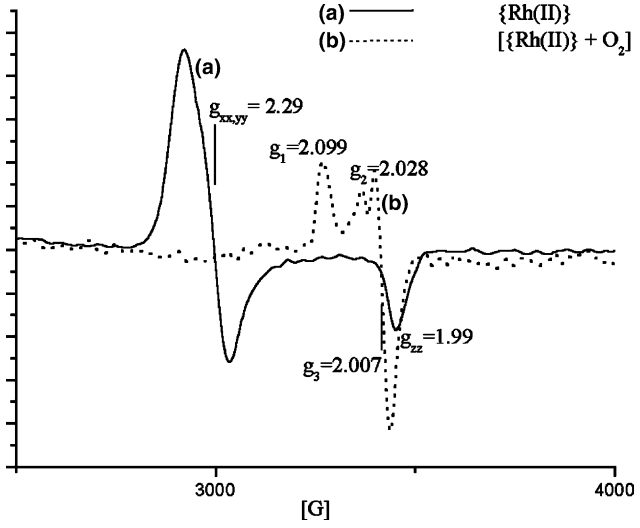


Fig. 2. ESR spectra (a) of $[RhL(PPh_3)_2]^{2+}$, [Rh(II)], in reaction mixture solution, in liquid nitrogen, (b) after reaction of [Rh(II)] with O_2.

ion, [Rh^{II}]. Bulky tertiary phosphines have been found to reduce rhodium(III) either by a two electron process to rhodium(I) or by one-electron reduction to rhodium(II), e.g., $RhCl_2(PBu^t_2R)_2$ (R = Me, Et, Pr^n) [33], $RhCl_2\{((o\text{-tol})_3P\}_2$ [34], $[Rh(PPh_3)_2Cl_2]$ [35], $[Rh(tmpp)_2](BF_4)_2$ (tmpp = 2,4,6-trimethoxyphenyl)phosphine [36]. Many Rh(II) complexes with N and N-O donor ligands have also been described [32b,37]. Cooling the reaction mixture in liquid nitrogen afforded a small amount of a yellow, unstable solid, whose IR spectrum displayed a strong band at 1640 cm^{-1}, characteristic for the acetyl group, as demonstrated for complexes $[RhBr_2(COCH_3)(CO)(PEt_2Ph)_2]$ (1667 cm^{-1}) and $[RhCl_2(COCH_3)(CO)(PEt_2Ph)_2]$ (1660 cm^{-1}) [38] and postulated for compounds $[M(CF_3COO)_2(CO)(PPh_3)_2]$ (M = Ru, Os), which have been found to be readily attacked by primary and secondary alcohols to liberate aldehydes and ketons, respectively, with concomitant formation of the hydride species $[MH(CF_3COO)(CO)(PPh_3)_2]$ [39].

The reaction performed in the presence of nitrogen gives a mixture of $[Rh(H)L(PPh_3)_2](ClO_4)_2$ (**1**) and $[Rh(CO)L(PPh_3)_2]ClO_4$ (**2**) in a ratio of ca. 5:1 (based on ^1H NMR spectra) under the reaction conditions described. Fractional crystallization, under vacuum, from the solution of $CHCl_3$/EtOH (1:1), affords **1** and **2** as individual solids, **2** precipitating as the first one.

The analogous reaction performed in an argon atmosphere leads to the formation of $[Rh(CO)L(PPh_3)_2](ClO_4)$ (**2**) as the main product. Some amounts of the compounds $[RhL_2](ClO_4)_3$ and $[RhL(H_2O)_2(ClO_4)](ClO_4)_2$ [27,28] as well as $OPPh_3$ were identified in the mother liquors.

The reaction solution, containing the [Rh(II)] moiety affected by oxygen, changes its colour from red to pale-yellow. Its ESR spectrum ($g_1 = 2.099$, $g_2 = 2.028$, $g_3 = 2.007$; $g_{av} = 2.045$) (Fig. 2(b)) is indicative of a superoxo Rh(III) derivative $[Rh^{III}(O_2^-)]^{2+}$ by comparison with literature data [29d,37c,37d,38,40–42]. Further stirring of the oxygenated solution under nitrogen flow for more then 20 h affords the hydride compound $[Rh(H)L(PPh_3)_2](ClO_4)_2$ (**1**).

The reaction performed in MeOH led only to the formation of **1**.

A reasonable explanation for the experimental observations is to suppose that in its interactions the rhodium(II) compound may follow a few different reaction pathways. The stability of Rh(III) ($4d^6$) or Rh(I) ($4d^8$) relative to Rh(II) ($4d^7$) allows easy one-electron oxidation or reduction reactions of Rh(II) intermediates to occur.

Thus it can be tentatively assumed that **1** is formed according to reaction (2), while the formation of **2** follows reactions (3) and/or (4).

$$2[Rh(II)] + C_2H_5OH \rightarrow 2[Rh^{III}H] + CH_3CHO \quad (2)$$

$$2[Rh(II)] + C_2H_5OH \rightarrow 2[Rh^{I}(CO)] + H_2 + CH_4 \quad (3)$$

$$[Rh(II)] + CH_3CHO \rightarrow [Rh^{I}(CO)] + CH_4 \quad (4)$$

The positive effect of oxygen on the formation of **1** suggests that the superoxide coordinated to the Rh centre acts as a base that abstracts H^+ from alcohol affording an acyl derivative subsequently converted to rhodium hydride (reaction 5). The base has been found to play a crucial role in the formation both of hydrides [38,43] and carbonyls [39] by dehydrogenation of alcohols. All the reported studies were carried out in strong acidic conditions. Thus, a plausible reaction is given by

$$[Rh(II)] + O_2 \rightarrow [Rh^{III}(O_2^-)] \xrightarrow[C_2H_5OH]{H^+} [Rh^{III}(H)] + CH_3COOH + H_2O \quad (5)$$

We have investigated appropriate chemical routes in an effort to isolate intermediate products.

The IR spectrum of **1**, in a Nujol mull, displays a band at 2180 cm^{-1}, which is assigned to Rh–H stretching vibration. This frequency falls within the range for Rh(III) hydrides, Table 1, [44–48].

Table 1
Spectral data for hydrido-complexes of rhodium(III)

Compound	ν(Rh–H) (cm^{-1})	δ_H	$J_{Rh,H}$ (Hz)	$J_{P,H}$ (Hz)	Reference
$[Rh(H)L(PPh_3](ClO_4)_2$	2180	−14.3	25.1	18.4	this work
cis-$[Rh(H)(Cl)L^1](ZnCl_4)$	2119	−20.70	36.4		[44]
trans-$[Rh(H)(Cl)L^1](ZnCl_4)$	2124	−20.34	34.4		[44]
$[Rh(H)(NH_3)_5](SO_4)$	2079	−17.1	14.5		[45]
$[Rh(H)(NH_3)_5](ClO_4)_2$	2126				[45]
trans-$[Rh(NH_3)_4(H_2O)(H)](SO_4)$	2146				[45]
trans-$[Rh(H)(en)_2Cl]^+$	2100	−21	31.0		[45]
cis-$[Rh(H)(en)_2Cl]^+$	2093	−21	31		[46]
cis-$[Rh(H)trienCl]^+$	2081	−18.8	27.0		[46]
$K_2[Rh(H)(CN)_4(H_2O)]$	1976				[47]
$[Rh(H)py_4Cl]Cl$	2000	−18.5			[48]

L^1 = [14] and N_4; triene = ethylenetetramine.

Table 2
IR ν(CO) and ^{13}C NMR data for rhodium(I) complexes

Compound	ν(CO) (cm^{-1})	Solvent	T (K)	δ(CO)	$^{1}J_{Rh,C}$ (Hz)	J_{CRhP} (Hz)	Reference
$[Rh(CO)L(PPh_3)_2]ClO_4$	2002[a] 2006[b]	CD_2Cl_2	243	189.1	68.5	17.0	this work
$[Rh(CO)(PPh_3)_2L^2]PF_6$	2001						[49]
$[Rh(CO)(PPh_3)_2L^3]PF_6$	2000						[49]
$[Rh(CO)(PPh_3)_2^4]PF_6$	2000						[49]
$[Rh(CO)(PPh_3)_2^5]PF_6$	2001						[49]
trans-$[Rh(CO)F(PPh_3)_2]$		CD_2Cl_2	243	190.6	68.8	16.8	[50]
trans-$[Rh(CO)(ONO_2)(PPh_3)_2]$	1982[c]	$CDCl_3$	243	190.6	74.7	16.9	[50]
trans-$[Rh(CO)Cl(PPh_3)_2]$	1979.5[c]	$CDCl_3$	243	187.8	74.3	16.0	[50]
trans-$[Rh(Sp)_2COCl]^{2-}$[d]		CH_3OH	298	187.8	74.5	15.8	[51]
$[Rh(Sp)COCl_2]^{2-}$		H_2O	298	184.7	79.7	17.0	[51]
$[Rh(acac)(Sp)CO]^{-}$		H_2O	298	189.5	76.3	24.0	[51]

[a] KBr.
[b] Nujol.
[c] THF solution, L^2 = imidazole, L^3 = benzimidazole, L^4 = 2-methylbenzimidazole, L^5 = 2-ethylbenzimidazole.
[d] Sp = $[PPh_2(C_6H_4SO_3]^{-}$.

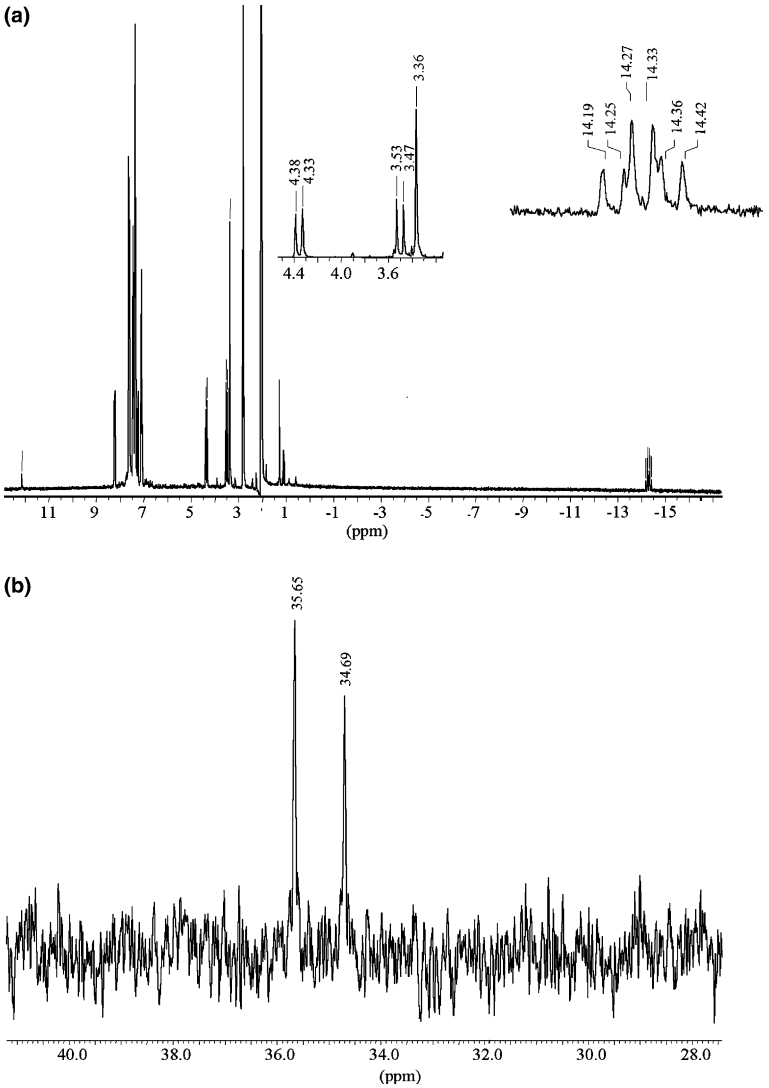


Fig. 3. NMR spectra of $[Rh(H)L(PPh_3)_2](ClO_4)_2$ (**1**) in acetone-d_6: (a) ^{1}H, (b) ^{31}P{H}.

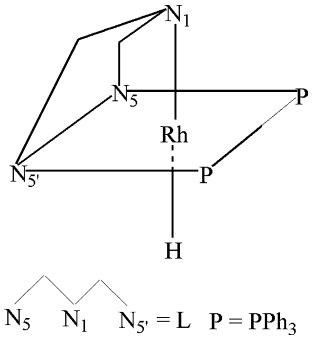


Fig. 4. Schematic structure of **1**.

The ν(Rh–H) frequency disappears when the spectrum is measured as KBr pellets. This indicates that the hydridic hydrogen is replaced by halide, giving most probably the halide complex $[RhBrL(PPh_3)_2](ClO_4)_2$. Replacement of hydrogen by halogen was found to take place easily for $[PtHCl(PEt_3)_2]$ [43].

A Rh–CO stretching vibration appears in the IR spectrum of **2** as a very strong band at 2002 cm^{-1}, which shifted to 2006 cm^{-1} in a Nujol mull (Table 2).

It has been reported that some rhodium(III) complexes in the presence of tertiary phosphines react with primary alcohols to give rhodium(I) carbonyl compounds, e.g., $[Rh(CO)(ONO_2)(PPh_3)_2]$ [51], *trans*-$[RhCl(CO)(PR_3)_2]$, ($PR_3 = PMe_2Ph$, PEt_2P, PEt_2Ph) [38].

3.2. NMR studies of *1* and *2*

The proton NMR of compound **1** (Fig. 3) in the hydridic region shows a quartet at −14.3 ppm. The presence of a quartet can be rationalized as being generated by the coupling between the hydrogen atom and

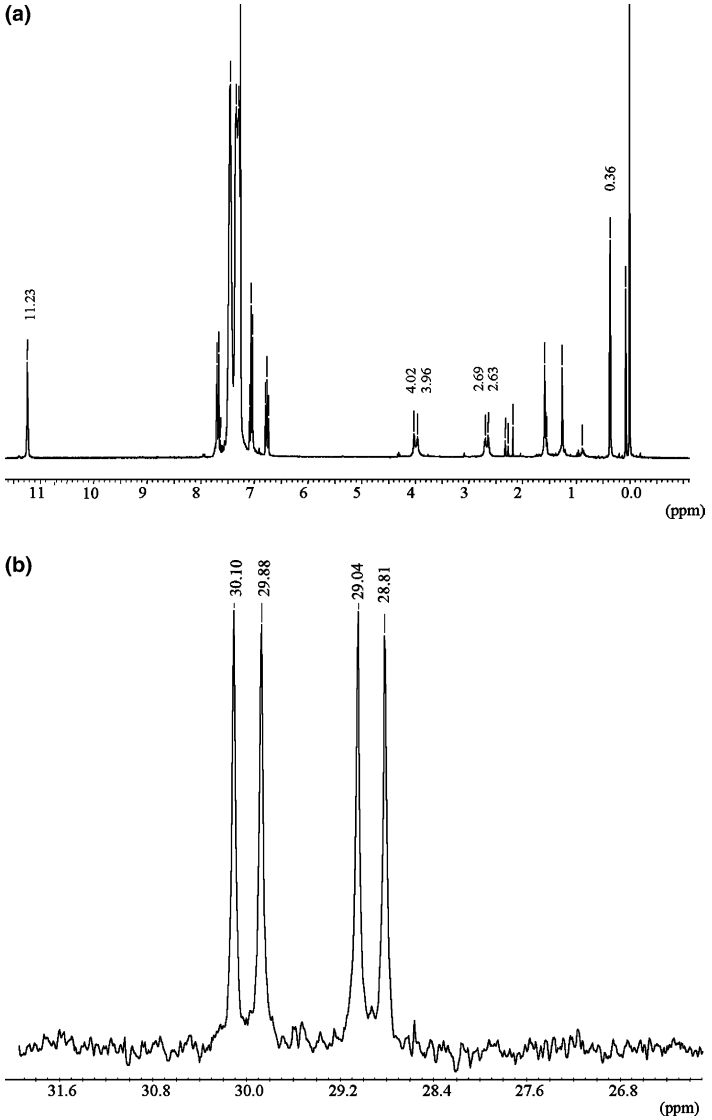


Fig. 5. MR spectra of $[Rh(CO)L(PPh_3)_2]ClO_4$ (**2**) in $CDCl_3$ (a) ^1H, (b) ^{31}P {H}, 298 K.

the two equivalent phosphorous atoms, giving rise to a triplet, which is further split by rhodium to form a triplet of doublets. The appearance of a quartet can then be explained by assuming that $J_{P,H}$ is almost equal to $J_{Rh,H}$. Actually, they are slightly unequal, as evidenced by shoulders seen on the individual peaks of the quartet. From the fine structure of that multiplet, the individual coupling constants were calculated to be $J_{P,H} = 18.4$ and $J_{Rh,H} = 25.1$ Hz. The latter was confirmed by a $^1H\{P\}$ NMR experiment, which resulted in the collapsing of the quartet into a doublet centred at −14.3 ppm. The $J_{Rh,H}$ value of 25.1 Hz indicates that two phosphine ligands are *cis*-coordinated to the hydride [52]. The 2- and 2′CH_2 resonances show an AB system with considerable magnetic non-equivalence of methylene protons ($\delta_a = 4.35$; $\delta_b = 3.52$ ppm with $J_{AB} = 16.5$ Hz). The additional singlet resonance from N_1CH_3 at 3.37 ppm, downfield shifted in comparison with the free ligand (3.27 ppm) [27,28], and an unresolved aromatic group of signals in a 7.0–7.6 ppm region from the ligands L and PPh_3 are consistent with the molecular structure of the complex with a facial L ligand, two axial phosphines, and the hydride ion *trans* to N_1 and *cis* to both phosphines. The $N_3H + N_{3'}H$ singlet resonance appears at 12.1 ppm.

The ^{31}P NMR spectrum (Fig. 3(b)) displays one doublet at 35.1 ppm with $^1J_{Rh,P} = 116$ Hz. This indicates that both PPh_3 ligands are equivalent and mutually *cis*.

Both ^1H and $^{31}P\{H\}$ NMR data are entirely in accord with the schematic structure of **1** in Fig. 4.

The ^1H and $^{31}P\{H\}$ NMR spectra of **2** in chloroform-d are presented in Fig. 5.

The characteristic features of **2** are the presence of an AB-type spectrum of methylene protons (C(2)–H_2 and

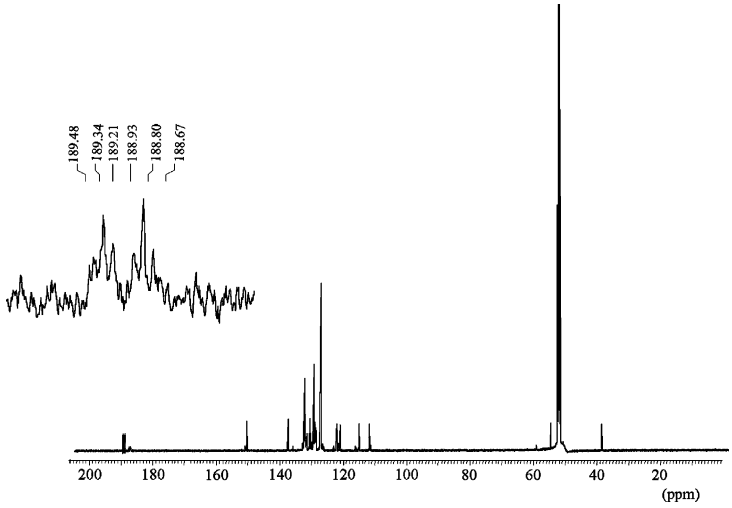


Fig. 6. $^{13}C\{H\}$ NMR spectrum of **2** in CD_2Cl_2 at 243 K.

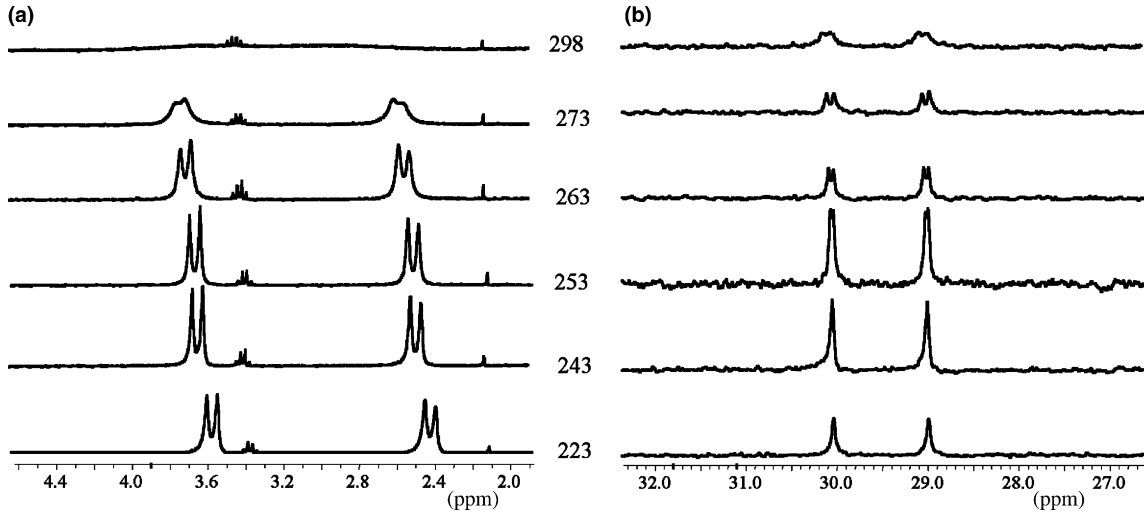


Fig. 7. Variable-temperature (a) ^1H and (b) $^{31}P\{H\}$ NMR spectra of **2** in CD_2Cl_2.

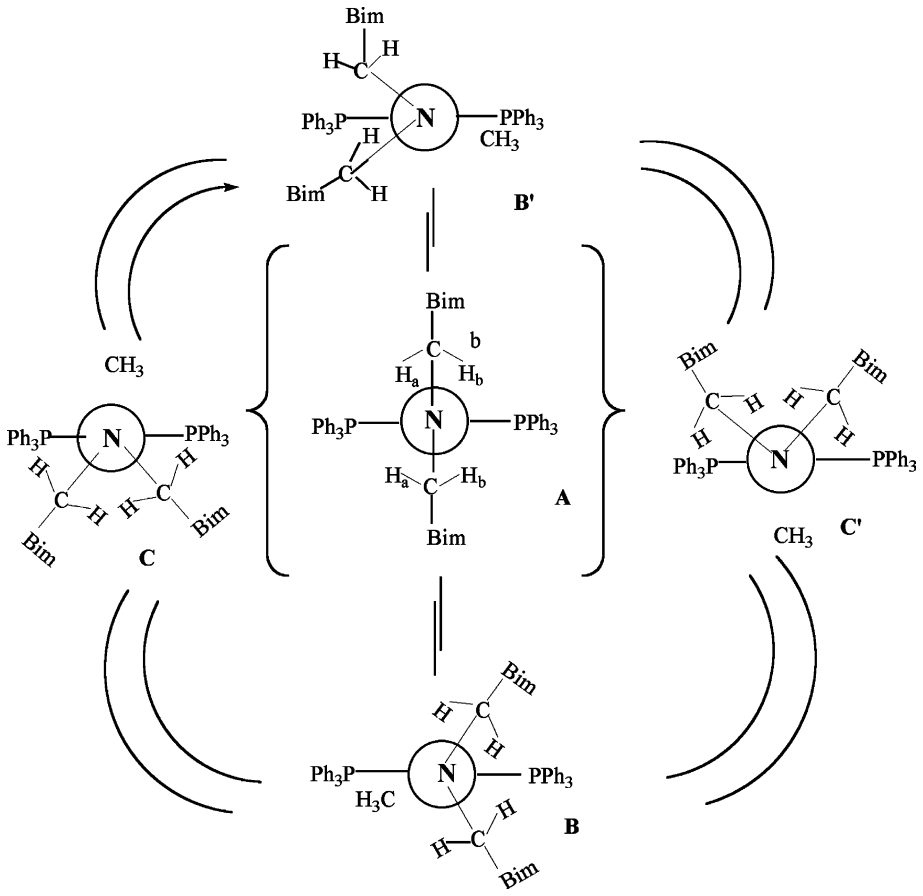


Fig. 8. Schematic representation of interconversions observed in variable-temperature NMR spectra of **2**.

C(2′)–H_2) and the concomitant presence of a doublet of doublets in the ^{31}P NMR spectrum. It is noteworthy that the N_1–CH_3 resonance ($\delta \approx 0.4$ ppm) is considerably upfield shifted in comparison with **1**. The presence of a doublet of triplets at 189.1 ppm with $J_{Rh-C} = 68.5$ Hz and $J_{CRhP} = 17$ Hz in the ^{13}C{H} NMR spectrum of **2** (Fig. 6), taken at 243 K in dichloromethane-d_2, corresponding to a carbonyl group, is indicative of rhodium(I) complexes in a square planar environment (Table 2) [50,51].

Thus, two phosphine ligands are equivalent in **2** and coordinated *cis* to the carbonyl ligand. The fourth coordination site is occupied by L, which is coordinated in symmetrical fashion (only one set of resonances from benzimidazolyl groups is observed). This implies that L serves as a monodentate ligand, coordinated with the central rhodium(I) through N_1 *trans* to a CO molecule. Varied coordination behaviour of multidentate *N*-heterocycles has been observed in [M(BbzIR$_2$py$_2$)]ClO_4 (R = H – 2,6-bisbenzimidazolyl)pyridine; R = Me – 2,6-bis(*N*-methylbenzimidazol)pyridine; M = Cu, Co) [26,53]. Such coordination results in flexibility of L, reflected in a dynamic behaviour observed in variable-temperature ^{1}H and ^{31}P NMR experiments (Fig. 7).

In dichloromethane-d_2, at 298 K, the methylene protons of **2** give one broad singlet resonance centred at about 3.2 ppm and a broad doublet at 29.2 ppm in ^{1}H and ^{31}P{H} NMR spectra, respectively. As the temperature drops below the coalescence point (298 K), the methylene proton signal splits into two separate broad singlets at 3.70 ppm and 2.63 ppm at 273 K in the ^{1}H NMR spectrum, and an additional splitting of components of the doublet in the ^{31}P{H} NMR spectrum is found, leading to a doublet of doublets ($\delta = 29.5$, $J_{P-Rh} = 128.8$ Hz, $J_{P-P} = 28.5$ Hz). Further decrease of temperature results in the sharpening of resonances of the typical AB pattern and disappearance of the P–P homonuclear splitting in the ^{31}P NMR spectrum, which eventually becomes a well-resolved doublet. The

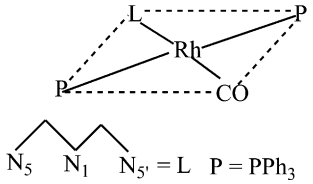


Fig. 9. Schematic structure of **2**.

Table 3
Isomerization and hydrogenation of olefins over the system $\{[Rh(H_2O)_6]^{3+} + L + PPh_3\}$ in 1 M $HClO_4$/EtOH solution

Olefin	Solvent	1-Hexene	Σ *cis*-,*trans*-2-Hexene	Hexane	Cyclohexene	Cycohexane
1-Hexene	EtOH	2.56	91.95	5.9		
	MeOH	25.26	74.74			
Cyclohexene	EtOH				95.61	4.39
	MeOH				99.0	0.47

$[Rh(H_2O)_6]^{3+} = 8 \times 10^{-3}$ M; $[L] = 8 \times 10^{-3}$ M; $[PPh_3] = 2.4 \times 10^{-2}$; [olefine] $= 8 \times 10^{-2}$; 348 K; 3 h; N_2. Further studies are underway.

described spectral change observed in dichloromethane can be attributed only to the conformational changes around the metal centre due to L. The central nitrogen atom N_1 in the free ligand has roughly sp^3-hybridization, with $C(CH_3)$–N(1)–C(2 or 2′) and C(2)–N(1)–C(2′) tetrahedral angles of ca. 104–110° [27,28]. It still remains sp^3-hybridized when coordinated through N(1) to rhodium(I). However, it interconverts rapidly with inversion of the configuration at N(1), as can be concluded from the coalescence of H_a and H_b resonances at 298 K. This interconversion between isomers B and B′ and/or C and C′ can be represented by form A as virtual average species observed at 298 K. When temperature goes down below 298 K, the forms B and B′ interconvert slowly on the NMR time-scale, the H_a and H_b protons are diastereotopic and an AB-type ^1H NMR spectrum is observed, and at the same time the phosphine ligands are non-equivalent and mutually coupled resulting in the presence of a doublet of doublets in the ^{31}P NMR spectrum. This situation takes place within the 283–263 K temperature range. Further decrease of temperature results in the disappearance of the non-equivalence of the phosphine ligands and the appearance of a sharp doublet in the ^{31}P NMR spectrum below 260 K. These spectra can be attributed to slowly interconverting forms C and C′, in which H_a and H_b protons are still diastereotopic (an AB-type spectrum is observed across the entire 263–233 K temperature range) and the phosphines become equivalent (Fig. 8).

In more polar solvents (chloroform, acetone) in comparison with methylene dichloride, the B $\Longleftrightarrow$ B′ interconversion is slow at 298 K on both the ^1H and ^{31}P NMR time-scales, and consequently the AB spectrum from C(2 and 2′)–H_2 in the ^1H and a doublet of doublets in ^{31}P NMR spectra are observed.

All the obtained data correspond to the formula of **2** and its proposed structure is depicted in Fig. 9.

The hydride **1** dissolves well in acetone, moderately in chloroform, methanol, and acetonitrile, and sparingly in ethanol. The carbonyl compound **2** dissolves well in chlorinated solvents, moderately in acetone, and sparingly in ethanol. Complexes **1** and **2** are stable in the solid state and in solutions under an inert atmosphere. Prolonged exposure of the solutions to air results in their decomposition. The IR spectrum exhibits vibrations at 540 and 727 cm^{-1} and the $^{31}P\{H\}$ spectrum shows a band at ca. 33 ppm, attributable to $OPPh_3$.

3.3. Catalytic activity

Preliminary studies indicated a double-bond migration to be a result of the interaction of the system consisting of $[Rh(H_2O)_6]^{3+}$, L, and PPh_3 with olefins, for reactions carried out in situ under a nitrogen atmosphere. Some hydrogen transfer and formation of saturated hydrocarbons were also observed (Table 3).

4. Conclusions

In this paper we have shown that reaction between $[Rh(H_2O)_6]^{3+}$ and L carried out in the presence of PPh_3 results in the formation of a metalloradical Rh(II) species. The data obtained implies that the observed dehydrogenation and decarbonylation of ethanol is effected by the latter. Both the hydride $[Rh(H)L(PPh_3)_2](ClO_4)_2$ (**1**) and the carbonyl $[Rh(CO)L(PPh_3)_2](ClO_4)$ (**2**) complexes have been isolated and determined. Dynamic properties of **2** evidence the ability of L to adapt its geometry to the electronic and geometric preferences of the metal centre. It may be beneficial for catalytic reactions to occur.

Acknowledgements

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