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Preparation of aryldiazene complexes of rhodium

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Abstract

Aryldiazene complexes $[Rh(ArN{=}NH)(CO)(PPh_3)_3]BF_4$ (**1**) and $[Rh(ArN{=}NH)(PPh_3)_4]BF_4$ (**2**) ($Ar = C_6H_5$ or $4\text{-}CH_3C_6H_4$) were prepared by allowing hydride species $RhH(CO)(PPh_3)_3$ and $RhH(PPh_3)_4$ to react with aryldiazonium cations at low temperature. The complexes were characterised by IR and ^1H-, ^{31}P- and ^{15}N-NMR spectra, using ^{15}N labelled compounds. Free aryldiazene ArN=NH species and $[Rh\{PPh(OEt)_2\}_4]BF_4$ were obtained by reacting the hydride $RhH[PPh(OEt)_2]_4$ with aryldiazonium cations in CH_2Cl_2 at − 80°C. Reactions of aryldiazene complexes **1** and **2** with H_2 (1 atm) were also studied, but did not lead to arylhydrazine derivatives. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium; Aryldiazene complexes; Free aryldiazene

1. Introduction

Currently there is a lot of interest in the chemistry of transition metal complexes containing aryldiazenido, ArN_2, aryldiazene, ArN=NH, or other partially reduced dinitrogen ligands, NH_x, not only due to possible relevance in the nitrogen fixation process, but also to the different coordination modes and to the interesting properties that this class of ligands may present [1,2]. However, the influence of various factors such as the nature of the central metal, its oxidation state, and the nature of the ancillary ligand on the properties of the complexes has not yet been completely rationalised [1]. Therefore, a systematic study of this class of complexes is desirable, in order to clarify the factors governing not only the wide range of coordination geometries adopted by these diazo ligands, but also their potential properties towards oxidation, reduction, protonation and deprotonation reactions.

In this context, we have reported several studies on the diazo chemistry of the iron triad [3], including the synthesis and reactivity of mono- and bis(aryldiazenido), aryldiazene and hydrazine derivatives. Parallel studies on the cobalt family involved the synthesis of the first aryldiazenido [4] $[Co(RN_2)\{PPh(OEt)_2\}_4](BPh_4)_2$, the reactivity of hydride $CoHP_4$ (P = phosphite) towards aryldiazonium salts [5], and the recent preparation of hydrazine complexes of iridium [6]. As an extension to these studies, we have now focused our attention to rhodium as the central metal, the diazo chemistry of which is less known when compared with that of other transition metals. In fact, while some examples of aryldiazenido complexes of the type $[RhCl(PPh_3)_2(p\text{-}N_2C_6H_4OMe)]BF_4$, $[RhC_6H_5P\{(CH_2)_3\text{-}P(C_6H_5)_2\}_2Cl(N_2C_6H_5)]PF_6$ are known [7,8], only one aryldiazene complex, $RhCl_3(ArN{=}NH)(PPh_3)_2$, has been described [9]. This paper reports a study on the reactivity of rhodium hydride complexes towards aryldiazonium cations, which allows the synthesis of a series of aryldiazene complexes to be obtained.

2. Experimental

2.1. General considerations and physical measurements

All synthetic work was carried out under an inert atmosphere using standard Schlenk techniques or a Vacuum Atmosphere dry-box. Once isolated, the complexes were found to be sufficiently stable in air to allow characterisation, but were stored under an inert

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atmosphere at −25°C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $RhCl_3 \cdot 3H_2O$ was a CHIMET product, used as received. Phenyldiethoxyphosphine, $PPh(OEt)_2$, was prepared by the method of Rabinowitz and Pellon [10] and purified by distillation under nitrogen. Diazonium salts $[ArN_2]^+BF_4^-$ were obtained in the usual way [11]. Labelled diazonium tetrafluoroborate $[C_6H_5N{\equiv}^{15}N]BF_4$ was prepared from $Na^{15}NO_2$ (99% enriched, CIL) and the appropriate amine. Alternatively, the $[C_6H_5^{15}N{\equiv}N]BF_4$ salt was obtained from $NaNO_2$ and $C_6H_5^{15}NH_2$. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna 750 FTIR spectrophotometer. NMR spectra (^1H, ^{31}P, ^{15}N) were obtained on a Bruker AC200 spectrometer at temperatures varying between −90 and +30°C, unless otherwise noted. ^1H spectra are referred to internal tetramethylsilane. $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. ^{15}N spectra refer to external $CH_3^{15}NO_2$, with downfield shifts considered positive. The SwaNMR software package [12] was used to treat NMR data. The conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 or 0°C were measured with a Radiometer CDM 83 instrument.

2.2. Synthesis of complexes

Hydride complexes $RhH(CO)(PPh_3)_3$, $RhH[PPh(OEt)_2]_4$, $RhH(PPh_3)_4$ were prepared following the methods previously reported [13–15].

2.2.1. [Rh(C$_6$H$_5$N=NH)(CO)(PPh$_3$)$_3$]BF$_4$ (**1a**), [Rh(4-CH$_3$C$_6$H$_4$N=NH)(CO)(PPh$_3$)$_3$]BF$_4$ (**1b**)

In a 25-cm^3 three-necked round-bottomed flask were placed 0.1 g (0.11 mmol) of $RhH(CO)(PPh_3)_3$ and an equimolar amount of the appropriate aryldiazonium tetrafluoroborate $(ArN_2)BF_4$ (0.11 mmol). The flask was cooled to −196°C and 10 cm^3 of CH_2Cl_2 added. The reaction mixture was brought to −5°C and stirred at this temperature for 50 min. The solvent was removed under reduced pressure, giving an oil which was treated, at −5°C, with 2 cm^3 of EtOH. By cooling of the resulting solution to −25°C yellow microcrystals were obtained which were filtered and dried under vacuum; yield ≥60%; Λ_M/S cm^2 mol^{-1} at 25°C = 87.3 for **1a**, 91.5 for **1b**. Anal. Found: C, 66.1; H, 4.5; N, 2.4. Calc. for $C_{61}H_{51}BF_4N_2OP_3Rh$ (**1a**): C, 66.0; H, 4.6; N, 2.5%. Anal. Found: C, 66.4; H, 4.6; N, 2.6. Calc. for $C_{62}H_{53}BF_4N_2OP_3Rh$ (**1b**): C, 66.2; H, 4.8; N, 2.5%.

2.2.2. [Rh(C$_6$H$_5$N=^{15}NH)(CO)(PPh$_3$)$_3$]BF$_4$ (**1a$_1$**), [Rh(C$_6$H$_5$^{15}N=NH)(CO)(PPh$_3$)$_3$]BF$_4$ (**1a$_2$**)

These complexes were prepared exactly like the related **1a** using labelled $(C_6H_5N{\equiv}^{15}N)BF_4$ and $(C_6H_5^{15}N{\equiv}N)BF_4$ aryldiazonium salts, respectively; yield ≥60%.

2.2.3. [Rh(C$_6$H$_5$N=NH)(PPh$_3$)$_4$]BF$_4$ (**2a**), [Rh(4-CH$_3$C$_6$H$_4$N=NH)(PPh$_3$)$_4$]BF$_4$ (**2b**)

A solid sample of $RhH(PPh_3)_4$ (0.1 g, 0.09 mmol) and an equimolar amount of the appropriate diazonium salt $(ArN_2)^+BF_4^-$ (0.09 mmol) were mixed together in a 25-cm^3 three-necked round-bottomed flask and cooled to −196°C. CH_2Cl_2 (10 cm^3) was added and the resulting mixture was brought to −5°C and stirred at this temperature for 2 h. The solvent was removed under reduced pressure to give an oil which was triturated, at −5°C, with Et_2O (5 cm^3). A yellow solid slowly separated out which was filtered and crystallised at −10°C from CH_2Cl_2 and Et_2O; yield ≥55%; Λ_M/S cm^2 mol^{-1} at 0°C = 79.4 for **2a**, 77.7 for **2b**. Anal. Found: C, 69.5; H, 4.8; N, 2.2. Calc. for $C_{78}H_{66}BF_4N_2P_4Rh$ (**2a**): C, 69.7; H, 4.9; N, 2.1%. Anal. Found: C, 69.9; H, 4.9; N, 2.0. Calc. for $C_{79}H_{68}BF_4N_2P_4Rh$ (**2b**): C, 69.8; H, 5.0; N, 2.1%.

2.2.4. [Rh(C$_6$H$_5$N=^{15}NH)(PPh$_3$)$_4$]BF$_4$ (**2a$_1$**), [Rh(C$_6$H$_5$^{15}N=NH)(PPh$_3$)$_4$]BF$_4$ (**2a$_2$**)

These complexes were prepared like the related **2a** using labelled $(C_6H_5N \equiv {}^{15}N)BF_4$ and $(C_6H_5^{15}N \equiv N)BF_4$ aryldiazonium salts, respectively; yield ≥55%.

2.2.5. [Rh{PPh(OEt)$_2$}$_4$]BF$_4$ (**3**)

In a 25-cm^3 three-necked round-bottomed flask were placed solid samples of $RhH[PPh(OEt)_2]_4$ (0.1 g, 0.11 mmol) and of an equimolar amount (0.11 mmol) of $(C_6H_5N_2)BF_4$ or $(4\text{-}CH_3C_6H_4N_2)BF_4$ aryldiazonium salts and the flask was cooled to −196°C. CH_2Cl_2 (10 cm^3) was added and the reaction mixture brought to −5°C and stirred for 1 h. The solvent was removed under reduced pressure giving an oil which was triturated with EtOH (5 cm^3). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallised from ethanol; yield ≥70%; Λ_M/S cm^2 mol^{-1} at 25°C = 84.3. Anal. Found: C, 48.7; H, 6.3. Calc. for $C_{40}H_{60}BF_4O_8P_4Rh$: C, 48.9; H, 6.2%.

2.2.6. Hydrogenation reactions

A solid sample of aryldiazene complex **1** or **2** (0.1 mmol) was placed in a 25-cm^3 three-necked round-bottomed flask cooled to −10°C and treated with 10 cm^3 of the appropriate solvent (CH_2Cl_2, THF). The resulting solution was allowed to stir under a hydrogen atmosphere (1 atm) for several hours (from 4 to 10) at −10°C, and the solvent was then removed under reduced pressure. The oil thus obtained was treated with EtOH (2 cm^3), giving a yellow solid which was filtered and dried under vacuum.

$$RhH(CO)(PPh_3)_3 + ArN_2^+BF_4^- \xrightarrow[-5\,^{\circ}C]{CH_2Cl_2} \underset{\mathbf{1}}{[Rh(ArN{=}NH)(CO)(PPh_3)_3]BF_4}$$

Scheme 1. Ar = C_6H_5 (**a**) or 4-$CH_3C_6H_4$ (**b**).

For the product obtained from **1a**: IR (KBr, cm^{-1}): 3277 (m), 3209 (m) [2008 (m), 1965 (s) ν(CO)]. ^{1}H-NMR (CD_2Cl_2-d_2, 293 K, δ ppm): 7.90–6.82 (m, Ph); 5.71 (br); 5.14 (br). $^{31}P\{^1H\}$-NMR (CD_2Cl_2-d_2, 293 K, δ ppm): 39–22 (m).

For the product obtained from **2a**: IR (KBr, cm^{-1}): 3285 (m), 3217 (m). ^{1}H-NMR (CD_2Cl_2-d_2, 293 K, δ ppm): 7.80–6.77 (m, Ph), 5.53 (m), 4.74 (m). $^{31}P\{^1H\}$-NMR (CD_2Cl_2-d_2, 293 K, δ ppm): 52–23 (m).

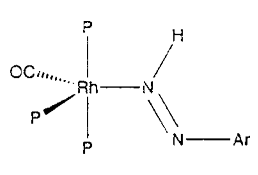
3. Results and discussion

The hydride–carbonyl complex $RhH(CO)(PPh_3)_3$ quickly reacts with aryldiazonium cations to give aryldiazene derivatives $[Rh(ArN{=}NH)(CO)(PPh_3)_3]BF_4$ **1**, which were isolated in good yield and characterised (Scheme 1).

Aryldiazene complexes **1** are rather unstable and only the use of low temperature at the start and during the reaction course allows stable compounds to be obtained. Furthermore, crucial for successful preparation of ArN=NH species is the use of an exact stoichiometric ratio between the reagents; otherwise, a large amount of decomposition substances are found in the final reaction product.

Analytical and spectroscopic data (Table 1) support the formulation of complexes **1**, which are air-stable yellow solids, thermally unstable in solution, and 1:1 electrolyte [16]. In particular, diagnostic for the presence of the diazene ligand was the high-frequency ^{1}H-NMR signal of the NH proton at 12.66–12.47 ppm, which is split into a sharp doublet in labelled compounds **1a$_1$** and **1a$_2$**. The values for both the $^1J_{^{15}NH}$ and $^2J_{^{15}NH}$ of 62 and 4.5 Hz, respectively, were also determined and agreed [1,3,9,17] with the proposed formulation.

The IR spectra show only one ν(CO) band at 1965 cm^{-1}. At room temperature, the $^{31}P\{^1H\}$-NMR spectra of **1** appear as rather broad multiplets, suggesting fluxionality of the complexes. In fact, lowering the sample temperature causes a change in the spectra, until at −90°C a well-resolved multiplet appears (Fig. 1), which may be simulated as the A_2B part of an AB_2X system (X = rhodium) with the parameters listed in Table 1. The structure of the complexes may be discussed in terms of a trigonal bipyramidal TBP or a square pyramidal SP geometry, but the spectroscopic data do not allow us to decide between them. However, a type **I** geometry, fitting both literature data [1,2] and IR and NMR spectra, may be tentatively proposed.



I

Geometry I

The synthesis of aryldiazene complexes **1** prompted us to extend the study on aryldiazonium cations to other rhodium hydrides of the type $RhHP_4$. The results obtained are summarised in Scheme 2.

Hydride $RhH(PPh_3)_4$ quickly reacts with aryldiazonium cations to give aryldiazene complexes $[Rh(ArN{=}NH)P_4]BF_4$ **2**, which were isolated in the solid state and characterised. Also in this case, crucial for the success of the synthesis was the use of stoichiometric amounts of the reagents and keeping temperature below −5°C during the reaction course. In fact, the use of a higher temperature yields decomposition products with only traces of aryldiazene complex.

In contrast, the hydride $RhHP_4$ containing the $PPh(OEt)_2$ ligand reacts in all conditions with aryldiazonium cations to give, instead of an aryldiazene complex, the tetrakis(phosphite) $[Rh\{PPh(OEt)_2\}_4]BF_4$ **3** derivative, which was isolated in high yield and characterised. The formation of a complex of type **3** suggested studying the reaction course extensively, starting from low temperature (−80°C), in order to detect the probable intermediate and to propose a path for the reaction. The ^{1}H-NMR spectrum of the solution containing $RhH[PPh(OEt)_2]_4$ and an equimolar amount of the aryldiazonium salt $ArN_2^+BF_4^-$ salt in CD_2Cl_2-d_2 at

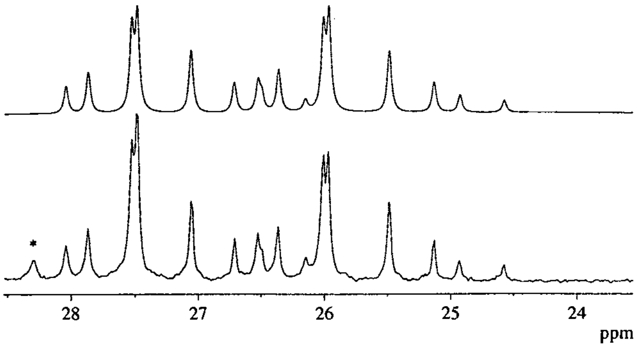


Fig. 1. $^{31}P\{^1H\}$-NMR spectra of complex $[Rh(4\text{-}CH_3C_6H_4N{=}NH)(CO)(PPh_3)_3]BF_4$ (**1b**) in CD_2Cl_2 at 203 K. Top: simulated (see parameters in Table 1); bottom: experimental. The peak indicated by an asterisk is due to an impurity.

Table 1
IR and NMR data for the rhodium complexes

	Compound	IR [a]		^{1}H-NMR [b,c]		Spin system	^{31}P{^{1}H}-NMR [b,d]
		$\bar{\nu}$ (cm^{-1})	Assignment	δ (J Hz)	Assignment		δ (J Hz)
1a	$[\mathrm{Rh(C_6H_5N{=}NH)(CO)(PPh_3)_3]BF_4}$	1965s	ν(CO)	12.66 (s)	$\mathrm{N}H$	$\mathrm{A_2BX}$ [e]	δ_A 26.9; $\delta_B = 25.9$; $J_{AB} = 38.3$; $J_{AX} = 122.2$; $J_{BX} = 128.3$
1a$_1$	$[\mathrm{Rh(C_6H_5N{=}^{15}NH)(CO)(PPh_3)]BF_4}$ [f]	1966s	ν(CO)	12.66 (d) $^1J_{15_{NH}} = 62$	$\mathrm{N}H$	$\mathrm{A_2BXY}$ [e]	$\delta_A = 26.9$;$\delta_B = 25.9$; $J_{AB} = 38.3$; $J_{AX} = 122.2$; $J_{BX} = 128.0$; $J_{AY} = <0.5$; $J_{BY} = <0.5$
1a$_2$	$[\mathrm{Rh(C_6H_5^{15}N{=}NH)(CO)(PPh_3)_3]BF_4}$	1965s	ν(CO)	12.67 (d) $^2J_{15_{NH}} = 4.5$	$\mathrm{N}H$	$\mathrm{A_2BXY}$ [e]	$\delta_A = 26.9$; $\delta_B = 25.9$; $J_{AB} = 38.3$; $J_{AX} = 122.2$; $J_{BX} = 128.0$; $J_{AY} = <0.5$; $J_{BY} = <0.5$
1b	$[\mathrm{Rh(4\text{-}CH_3C_6H_4N{=}NH)(CO)(PPh_3)_3]BF_4}$	1966s	ν(CO)	12.47 (s) 2.28 (s)	$\mathrm{N}H$ $\mathrm{C}H_3$	$\mathrm{A_2BX}$ [e]	$\delta_A = 26.9$; $\delta_B = 25.9$; $J_{AB} = 38.5$; $J_{AX} = 122.5$; $J_{BX} = 128.0$
2a	$[\mathrm{Rh(C_6H_5N{=}NH)(PPh_3)_4]BF_4}$			12.15 (m, br) [g]	$\mathrm{N}H$		29.6 (s, br) [g]; 50–21 (m, br) [e]
2a$_1$	$[\mathrm{Rh(C_6H_5N{=}^{15}NH)(PPh_3]_4BF_4}$ [h]			12.17 (dm) [g], $^1J_{15_{NH}} = 60$	$\mathrm{N}H$		50–21 (m, br) [e]
2a$_2$	$[\mathrm{Rh(C_6H_5^{15}N{=}NH)(PPh_3]_4BF_4}$			12.17 (m, br) [g]	$\mathrm{N}H$		28.3 (s, br) [g]
2b	$[\mathrm{Rh(4\text{-}CH_3C_6H_4N{=}NH)(PPh_3]_4BF_4}$			11.8 (m, br) [g] 2.32 (s)	$\mathrm{N}H$ $\mathrm{CH_3}$		28.5 (s, br) [g]; 50–20 m[e]
3	$[\mathrm{Rh\{PPh(OEt)_2\}_4]BF_4}$			3.56 (m), 3.27 (m), 1.04 (t)	$\mathrm{C}H_2$ $\mathrm{C}H_3$	$\mathrm{A_4X}$	δ_A 145.0; $J_{AX} = 180$

[a] In KBr pellets.

[b] In $\mathrm{CD_2Cl_2}$ at 25°C.

[c] Phenyl proton resonances are omitted.

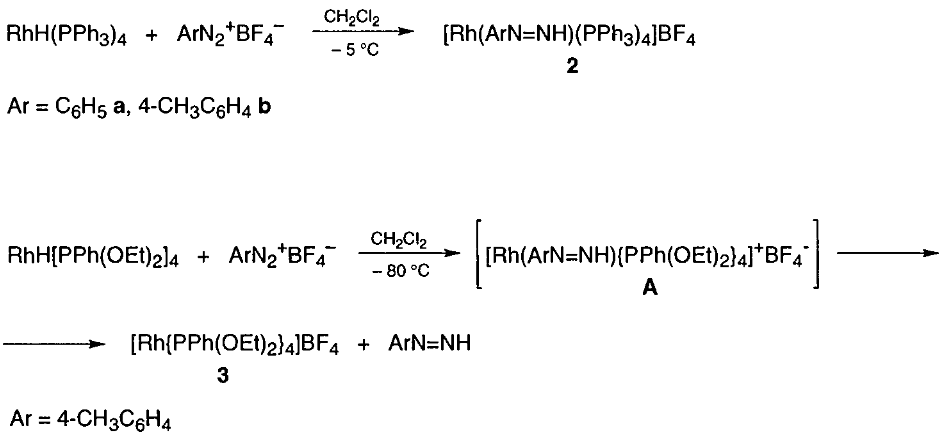
[d] Positive shift downfield from 85% $\mathrm{H_3PO_4}$.

[e] At −80°C.

[f] ^{15}N-NMR, δ: 3.9 (dd), $J_{^{15}NRh} = 12$ Hz, $J_{^{15}NH} = 62$ Hz.

[g] At −5°C.

[h] ^{15}N-NMR, δ: −20 (s, br).



Scheme 2.

− 80°C shows a diazene proton signal at 15.29 ppm, which is split into a doublet ($^1J_{^{15}\mathrm{NH}} = 49.9$ Hz) using the labelled ArN ≡ $^{15}N^+BF_4^-$ salt, and may suggest the presence of an aryldiazene complex. However, the $^{31}P\{^1H\}$-NMR spectra of this reaction mixture do not, in any conditions, show the presence of new signals beside the two doublets due to the final $[Rh\{PPh(OEt)_2\}_4]^+$ cations **3** (at 145.2 ppm) and the starting $RhH[PPh(OEt)_2]_4$ derivative at 166.9 ppm. These results are rather surprising and may be explained by the formation of an aryldiazene intermediate $[Rh(ArN{=}NH)P_4]^+$ [**A**], in which the ArN=NH ligand is so labile even at − 80°C so as to give $[Rh\{PPh(OEt)_2\}_4]^+$ and the free ArN=NH ligand (Scheme 2). Comparison of the value of the chemical shift of the NH diazene proton signal with those of already known examples of free aryldiazene molecules [18] supports its formation and shows that also the hydrides containing the phosphonite $PPh(OEt)_2$ undergo an insertion reaction of ArN_2^+ cation into the Rh–H bond giving an aryldiazene complex. The lability of the ligand, however, makes this reaction useful as a new method for the easy synthesis, even at very low temperatures, of aryldiazene molecules. The reaction was also followed at temperature higher than − 80°C and observed a slow decomposition of free aryldiazene (upon 0°C) giving N_2 and the corresponding hydrocarbon $CH_3C_6H_5$.

Previously reported methods [18] for the synthesis of these thermally unstable ArN=NH molecules often involve substitution reactions of coordinate ArN=NH species at a temperature (between − 5 and + 5°C) at which the free aryldiazene is only marginally stable. The use of the reaction of $RhH[PPh(OEt)_2]_4$ with ArN_2^+ allows the easy synthesis of ArN=NH in good yield at low temperature, and it can be used as a reagent for peculiar organic reactions.

Results on the reactivity of phosphite-containing rhodium(I) hydrides $RhHP_4$ with aryldiazonium cations allow comparisons with the reactivity of the related cobalt complexes $CoH[PPh(OEt)_2]_4$, previously reported by us [5]. Reactivity with ArN_2^+ is completely different in the two cases, with the oxidation of $CoH[PPh(OEt)_2]_4$ to give cationic paramagnetic $[CoH\{PPh(OEt)_2\}_4]^+$ species for cobalt, and insertion of ArN_2^+ into the Rh–H bond to give an aryldiazene for rhodium. This different behaviour in the reactivity of the two hydrides towards ArN_2^+ is difficult to explain, also taking into account that it is very rare [1,19] for aryldiazonium salt to act as an oxidant on a metal complex. Probably, the unreactivity toward insertion of the $CoHP_4$ is due to the low hydridic character of the H^- ligand in cobalt complexes, which prevents reduction of ArN_2^+ to aryldiazene. Instead, oxidation of the central metal from + 1 to + 2 was observed, which is probably peculiar to this metal, but does not involve all the hydrides in the triad, for which the classical insertion reaction to give aryldiazene complexes predominates [1,2,6].

The yellow–orange $[Rh(ArN{=}NH)(PPh_3)_4]BF_4$ **2** complexes are stable as solids, but decompose in solution even at 0°C, with loss of the aryldiazene ligand. Therefore, spectroscopic measurements for characterisation (^1H- and ^{31}P-NMR) were carried out at temperatures below 0°C. Conductivity measurements were also carried out at 0°C and indicated the presence of 1:1 electrolytes [16]. The ^1H-NMR spectra are consistent with the presence of the aryldiazene ligand, showing in the high frequency region a broad NH signal at 12.15 ppm for **2a** (at 11.8 ppm for **2b**), split into a sharp doublet ($^1J_{^{15}\mathrm{NH}} = 60$ Hz) in the labelled $[Rh(PhN{=}^{15}NH)(PPh_3)_4]BF_4$ **2a$_1$** compound, in agreement with the proposed formulation. At − 5°C, the $^{31}P\{^1H\}$-NMR spectra appear as a broad signal which changes as the temperature is lowered. However, even at − 90°C the spectra are still too broad to give a fine structure, thus preventing geometric assignment in solution for these complexes.

The tetracoordinate $[Rh\{PPh(OEt)_2\}_4]BF_4$ is a yellow diamagnetic solid, stable in the air, and 1:1 electrolyte [16]. The analytical and spectroscopic data (Table 1) confirm its formulation, which is similar to other known [20] tetrakis(phosphite) Rh(I) complexes.

Aryldiazene complexes of rhodium **1** and **2** were reacted with H_2 (1 atm) in order to test the possibility of reduction of the ArN=NH moiety to hydrazine. We carried out the reaction of **1** and **2** with H_2 in various solvents and at low temperature (−10 to 0°C) to avoid decomposition of the starting complexes. A yellow–orange solid was obtained from the reduction of both complexes **1** and **2**, whose IR spectra show two medium intensity bands at 3277 and 3209 cm^{-1} for reduction of **1** and at 3285 and 3217 cm^{-1} for reduction of **2**, probably attributable to $\nu(NH)$ of a coordinated arylhydrazine ligand. The ^1H-NMR spectra of this reduction product show the presence of two broad signals between 5.71 and 4.74 ppm, attributable to NH and NH_2 signals of an arylhydrazine ligand. On this basis, it seems reasonable to hypothesise that the reaction proceeds with reduction of the aryldiazene ligand to arylhydrazine in mild conditions. In order to confirm the formulation of the reduction product, we treated the labelled complex $[Rh(PhN{=}^{15}NH)(CO)P_3]BF_4$ **1a₁** with H_2 and recorded the ^1H-NMR spectra of the resulting solid. Surprisingly, the spectra were exactly like those of the unlabelled complex, and no splitting due to coupling with ^{15}N of the signals attributable to NH and NH_2 was observed. We repeated the reaction with the other labelled complexes $\mathbf{1a_2}$, $\mathbf{2a_1}$ and $\mathbf{2a_2}$ and observed no variations in the proton spectra, in comparison with those of the unlabelled ones, indicating that the broad signals at 5.71–4.74 ppm are not attributable to the NH proton of hydrazine complexes. We also attempted to purify the complexes, and observed that crystallisation from CH_2Cl_2 and EtOH gives a product with identical ^1H-NMR spectra, but whose IR spectra show the disappearance of the 3285–3209 cm^{-1} band attributed to the $\nu(NH)$ group. On this basis, and taking into account that elemental analyses indicate the absence of N_2, we can exclude the possibility that the reaction of rhodium(I) aryldiazene **1** and **2** with H_2 proceeds with the reduction of the ArN=NH group, to give an arylhydrazine complex. These results contrast with previous studies [21] on the diazo chemistry of rhodium, which reported that aryldiazene and aryldiazenido complexes may be reduced to arylhydrazine complexes in the presence of H_2 in mild conditions (1 atm, 20°C). We also attempted to assign a formula to our reduction product, but the ^{31}P spectra indicate the presence of more than one product, and we can therefore only conclude that, in the presence of H_2, the aryldiazene complexes of rhodium **1** and **2** react with loss of the nitrogen ligand and formation of uncharacterised products.

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