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Preparation of bis(aryldiazene) and new aryldiazenido complexes of rhenium

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Abstract

Mixed-ligand hydride $ReH_2(NO)L(PPh_3)_2$ complexes [L = $P(OEt)_3$ or $PPh(OEt)_2$] were prepared by allowing the $ReH_2(NO)(PPh_3)_3$ species to react with an excess of phosphite. Treatment of $ReH_2(NO)L(PPh_3)_2$ hydrides with an equimolar amount of aryldiazonium cations ArN_2^+ gives the mono-aryldiazene $[ReH(ArN{=}NH)(NO)L(PPh_3)_2]BPh_4$ complexes (Ar = C_6H_5, 4-$CH_3C_6H_4$), while treatment with an excess of ArN_2^+ yields bis(aryldiazene) $[Re(ArN{=}NH)_2(NO)L(PPh_3)_2](BPh_4)_2$ derivatives. Binuclear $[\{ReH(NO)L(PPh_3)_2\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)](BPh_4)_2$ and $[\{Re(4\text{-}CH_3C_6H_4N{=}NH)(NO)L(PPh_3)_2\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)](BPh_4)_4$ complexes (Ar–Ar = 4,4′-C_6H_4–C_6H_4, 4,4′-C_6H_4–CH_2–C_6H_4) were also prepared. The reaction of the triphenylphosphine $ReH_2(NO)(PPh_3)_3$ complex with aryldiazonium cations was studied and led exclusively to mono-aryldiazene $[ReH(ArN{=}NH)(NO)(PPh_3)_3]BPh_4$ and $[\{ReH(NO)(PPh_3)_3\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)](BPh_4)_2$ derivatives. The complexes were characterised spectroscopically (IR, NMR) using the ^{15}N-labelled derivatives. The aryldiazenido $[ReH(C_6H_5N_2)\{PPh(OEt)_2\}_4]BPh_4$ complex was prepared by allowing trihydride $ReH_3[PPh(OEt)_2]_4$ to react with phenyldiazonium tetrafluoroborate. A reaction path involving the aryldiazene $[ReH_2(C_6H_5N{=}NH)\{PPh(OEt)_2\}_4]^+$ intermediate was also proposed.

Keywords: Rhenium; Hydride complexes; Bis(aryldiazene); Aryldiazenido; Phosphite ligands

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1. Introduction

Although the diazo chemistry of rhenium has been widely studied in the past 25 years, relatively few complexes with the aryldiazene ArN=NH ligand have been reported [1–3], and none containing two ArN=NH groups bonded to the same rhenium central metal have ever been described. Bis(aryldiazene) compounds are rare and were prepared [4] for the iron triad by double insertion of two ArN_2^+ into the M–H bond of appropriate MH_2L_4 hydrides.

Interest in the chemistry of these diazo complexes stems not only from their relevance in the dinitrogen fixation process [5], but also from the diverse reactivity modes and structural properties that this class of complexes may exhibit [1,2].

We have been active in this research area since 1984 and have reported several studies on the synthesis and the reactivity of aryldiazene, aryldiazenido and hydrazine complexes of d^6-transition metals [6], including the preparation of mono-aryldiazene $[Re(ArN{=}NH)(CO)_nL_{5-n}]BPh_4$ (L = phosphites, n = 1, 2, 3, 4) complexes of rhenium [3]. The poor reactivity of these diazene complexes along with the interesting properties shown by the known bis(aryldiazene) derivatives [4] prompted us to extend those studies to the preparation of bis(aryldiazene) derivatives of rhenium. The strategy we thought to use involved the reaction of rhenium dihydrides with aryldiazonium salts, in an attempt to achieve a double insertion into the two Re–H bonds. However, since the known dihydride [7] $ReH_2(NO)(PPh_3)_3$ does not give the bis(insertion) of ArN_2^+, we first investigated the synthesis of new hydrides and then the reaction with aryldiazonium cations. The results of these studies, which involve the synthesis of bis(aryldiazene) and new aryldiazenido complexes of rhenium, are reported here.

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2. Experimental

2.1. General considerations and physical measurements

All synthetic work was carried out in an inert atmosphere using standard Schlenk techniques or a Vacuum Atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored in an inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. Metallic rhenium was a Chempur product, used as received. The phosphite $P(OEt)_3$ (Aldrich) was purified by distillation under nitrogen; $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon [8]. Diazonium salts were obtained in the usual way [9]. The related bis(diazonium) salts $[N_2Ar{-}ArN_2](BF_4)_2$ ($Ar{-}Ar = 4,4'\text{-}C_6H_4{-}C_6H_4$, $4,4'\text{-}C_6H_4{-}CH_2{-}C_6H_4$) were prepared by treating the amine precursors $H_2NAr{-}ArNH_2$ with $NaNO_2$ as described for common mono-diazonium salts [9]. The labelled diazonium tetrafluoroborate $[C_6H_5N{\equiv}{}^{15}N]BF_4$ and $[4,4'\text{-}{}^{15}N{\equiv}NC_6H_4{-}C_6H_4N{\equiv}{}^{15}N](BF_4)_2$ were 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 prepared 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 FT-IR spectrophotometer. NMR spectra (^1H, ^{31}P) were obtained on a Bruker AC200 or an AVANCE 300 spectrometers at temperatures varying between −90 and +30 °C, unless otherwise noted. ^1H spectra are referred to internal tetramethylsilane. Phenyl proton resonances are omitted. $^{31}P\{^1H\}$ 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 conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C was measured with a Radiometer CDM 83 instrument.

2.2. Synthesis of complexes

Hydrides $ReH_2(NO)(PPh_3)_3$ and $ReH_3\{PPh(OEt)_2\}_3$ were prepared following the methods previously reported [7,10].

2.2.1. $ReH_2(NO)\{P(OEt)_3\}(PPh_3)_2$ and $ReH_2(NO)\{PPh(OEt)_2\}(PPh_3)_2$

An excess of the appropriate phosphite (6 mmol) was added to a solution of $ReH_2(NO)(PPh_3)_3$ (1 mmol, 1.0 g) in 20 cm^3 of toluene and the reaction mixture refluxed for 1 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 cm^3). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield = 85%. For $ReH_2(NO)\{P(OEt)_3\}(PPh_3)_2$: Found: C, 55.6; H, 5.3; N, 1.5. $C_{42}H_{47}NO_4P_3Re$ requires C, 55.50; H, 5.2; N, 1.5%. For $ReH_2(NO)\{PPh(OEt)_2\}(PPh_3)_2$: Found: C, 58.9; H, 5.1; N, 1.6. $C_{46}H_{47}NO_3P_3Re$ requires C, 58.7; H, 5.0; N, 1.5%.

2.2.2. $[ReH(ArN{=}NH)(NO)L(PPh_3)_2]BPh_4$ (*1* and *2*) [$L = P(OEt)_3$ (*1*), $PPh(OEt)_2$ (*2*), $Ar = C_6H_5$ (*a*), $4\text{-}CH_3C_6H_4$ (*b*)]

In a 25-cm^3 three-necked round-bottomed flask were placed solid samples of the appropriate hydride $ReH_2(NO)L(PPh_3)_2$ (0.1 mmol) and of the aryldiazonium salt $[ArN_2]BF_4$ (0.1 mmol). The flask was cooled to −196 °C and 10 cm^3 of CH_2Cl_2 added. The reaction mixture was brought to 0 °C, stirred for 1 h and then the solvent was removed under reduced pressure. The oil obtained was treated with ethanol containing an excess of $NaBPh_4$ (0.2 mmol, 68 mg) and the resulting solution stirred until a yellow solid separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield = 65%; Λ_M (S cm^2 mol^{-1}) = 50.2 for **1a**, 53.6 for **2a**, 49.9 for **2b**. Found: C, 65.0; H, 5.6; N, 3.2. $C_{72}H_{72}BN_3O_4P_3Re$ (**1a**) requires C, 64.9; H, 5.4; N, 3.15. Found: C, 67.1; H, 5.45; N, 3.2%. $C_{76}H_{72}BN_3O_3P_3Re$ (**2a**) requires C, 66.9; H, 5.3; N, 3.1. IR (KBr, cm^{-1}): 1882 (w) ν(ReH), 1674 (s) ν(NO). ^1H-NMR (CD_2Cl_2-d_2, 25 °C, δ): 13.08 (s, br), 11.50 (br) (NH), 3.81 ($J_{PH} = 8$ Hz), 3.65 ($J_{PH} = 8$ Hz) (q, ReH), 3.31, 3.29 (qnt, CH_2), 1.19, 0.78 (t, CH_3) ppm. $^{31}P\{^1H\}$-NMR (CD_2Cl_2-d_2, 25 °C, δ): AB_2 spin system, δ_A 131.1 ppm, δ_B 17.1 ppm, $J_{AB} = 18.3$ Hz; AB_2 spin system, δ_A 137.7 ppm, δ_B 24.1 ppm, $J_{AB} = 10.8$ Hz. Found: C, 67.2; H, 5.5; N, 3.20. $C_{77}H_{74}BN_3O_3P_3Re$ (**2b**) requires C, 67.05; H, 5.4; N, 3.05%. IR (KBr, cm^{-1}): 1871 (w) ν(ReH), 1682 (s) ν(NO). ^1H-NMR (CD_2Cl_2-d_2, 25 °C, δ): 12.89, 11.2 (s, br, NH), AB_2X spin system, δ_X 3.83, $J_{AX} = 10.1$ Hz, $J_{BX} = 3.30$ Hz; AB_2X spin system, δ_X 3.67, $J_{AX} = J_{BX} = 7.1$ Hz (ReH), 3.40–3.00 (m, CH_2), 2.37, 2.31 (s, CH_3), 0.94, 0.78 (t, CH_3 phos) ppm. $^{31}P\{^1H\}$-NMR (CD_2Cl_2-d_2, 25 °C, δ): AB_2 spin system, δ_A 131.5 ppm, δ_B 17.2 ppm, $J_{AB} = 18.3$ Hz; AB_2 spin system, δ_A 137.7 ppm, δ_B 24.1 ppm, $J_{AB} = 9.8$ Hz.

2.2.3. $[ReH(C_6H_5N{=}{}^{15}NH)(NO)L(PPh_3)_2]BPh_4$ (*1a₁* and *2a₁*) [$L = P(OEt)_3$ (*1*), $PPh(OEt)_2$ (*2*)]

These complexes were prepared exactly like the related unlabelled compounds **1a** and **2a** using $[C_6H_5N{\equiv}{}^{15}N]BF_4$ as a reagent; yield = 60%. For **2a$_1$**: IR (KBr, cm^{-1}): 1883 (w) ν(ReH), 1680 (s) ν(NO). ^1H-NMR (CD_2Cl_2-d_2, 25 °C, δ): 13.09 (dd, $^1J_{^{15}NH} = 62$ Hz, $^2J_{PH} = 4$ Hz), 11.49 (d, br, $^1J_{^{15}NH} = 61$ Hz) (NH), 3.80 (m), 3.64 (q) (ReH), 3.29, 3.14 (m, CH_2), 0.98, 0.81 (t, CH_3) ppm. $^{31}P\{^1H\}$-NMR (CD_2Cl_2-d_2, 25 °C, δ): AB_2Y spin system, δ_A 131.1 ppm, δ_B 17.1 ppm, $J_{AB} = 18.1$ Hz, $J_{AY} = 34.4$ Hz, $J_{BY} = 1.6$ Hz; AB_2Y spin system, δ_A

137.7 ppm, δ_B 24.2 ppm, $J_{AB} = 10.2$ Hz, $J_{AY} = 3.7$ Hz, $J_{BY} = 3.8$ Hz).

2.2.4. *[{ReH(NO)L(PPh_3)$_2$}$_2$(μ-HN=NAr–ArN=NH)](BPh_4)$_2$ (**3** and **4**) [L = P(OEt)$_3$ (**3**), PPh(OEt)$_2$ (**4**), Ar–Ar = 4,4′-C_6H_4–C_6H_4 (**c**), 4,4′-C_6H_4–CH_2–C_6H_4 (**d**)]*

In a 25-cm^3 three-necked round-bottomed flask were placed solid samples of the appropriate hydride $ReH_2(NO)L(PPh_3)_2$ (0.1 mmol) and of the bis(aryldiazonium)tetrafluoborate $[N_2Ar–ArN_2](BF_4)_2$ (0.05 mmol) and the flask was cooled to −196 °C. Methylene chloride (10 cm^3) was added and the reaction mixture, brought to 0 °C, was stirred for 4 h. The solvent was removed under reduced pressure to give an oil, which was treated with ethanol (3 cm^3). The addition of $NaBPh_4$ (0.2 mmol, 68 mg) in 2 cm^3 of ethanol caused the separation of a yellow solid which was filtered and crystallised from CH_2Cl_2 and ethanol; yield = 65%; Λ_M (S cm^2 mol^{-1}) = 121.5 for **3d**, 127.3 for **4c**, 123.9 for **4d**. Found: C, 64.9; H, 5.6; N, 3.2. $C_{145}H_{144}B_2N_6O_8P_6Re_2$ (**3d**) requires C, 65.0; H, 5.4; N, 3.15%. IR (KBr, cm^{-1}): 1890 (w) ν(ReH), 1695 (s) ν(NO). ^{1}H-NMR (CD_2Cl_2-d_2, 25 °C, δ): 12.88 (d, br), 11.5 (s, br) (NH), 3.98 (q, $^2J_{PH} = 8$ Hz, ReH), 3.77, 3.35 (qnt, CH_2), 1.03, 0.80 (t, CH_3) ppm. ^{31}P{^{1}H}-NMR (CD_2Cl_2-d_2, 25 °C, δ): AB_2 spin system, δ_A 107.0 ppm, δ_B 18.4 ppm, $J_{AB} = 24.1$ Hz; AB_2 spin system, δ_A 113.5, δ_B 24.1, $J_{AB} = 12.6$ Hz. Found: C, 67.10; H, 5.4; N, 3.2. $C_{152}H_{142}B_2N_6O_6P_6Re_2$ (**4c**) requires C, 66.9; H, 5.25; N, 3.1%. Found: C, 66.9; H, 5.5; N, 3.2. $C_{153}H_{144}B_2N_6O_6P_6Re_2$ (**4d**) requires C, 67.00; H, 5.3; N, 3.1%. IR (KBr, cm^{-1}): 1890 (w) ν(ReH), 1684 (s) ν(NO). ^{1}H-NMR (CD_2Cl_2-d_2, 25 °C, δ): 13.0, 11.4 (s, br, NH), 3.8 (m, ReH), 3.83 (s, CH_2), 3.31, 3.15 (qnt, CH_2 phos), 1.15, 0.82 (t, CH_3) ppm. ^{31}P{^{1}H}-NMR (CD_2Cl_2-d_2, 25 °C, δ): AB_2 spin system, δ_A 131.0 ppm, δ_B 17.2 ppm, $J_{AB} = 18.1$ Hz; AB_2 spin system, δ_A 137.6 ppm, δ_B 24.1 ppm, $J_{AB} = 9.6$ Hz).

2.2.5. *[Re(ArN=NH)$_2$(NO)L(PPh_3)$_2$](BPh_4)$_2$ (**5** and **6**) [L = P(OEt)$_3$ (**5**), PPh(OEt)$_2$ (**6**), Ar = C_6H_5 (**a**), 4-$CH_3C_6H_4$ (**b**)]*

An excess of aryldiazonium tetrafluoroborate $[ArN_2]BF_4$ (0.4 mmol) and the appropriate hydride $ReH_2(NO)L(PPh_3)_2$ (0.1 mmol) were placed as solid samples in a 25-cm^3 three-necked round-bottomed flask. The flask was cooled to −196 °C and dichloromethane (10 cm^3) added. The reaction mixture was brought to 0 °C, stirred for 3 h and then the solvent removed under reduced pressure. The oil obtained was treated with ethanol (3 cm^3) containing an excess of $NaBPh_4$ (0.4 mmol, 0.137 g) and the resulting solution stirred for 30 min. A yellowish-orange solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield = 60%; Λ_M (S cm^2 mol^{-1}) = 120.7 for **5a**, 114.8 for **5b**, 122.3 for **6a**, 117.5 for **6b**. Found: C, 69.9; H, 5.7; N, 4.1. $C_{102}H_{97}B_2N_5O_4P_3Re$ (**5a**) requires C, 69.70; H, 5.6; N, 4.0%. Found: C, 70.2; H, 5.8; N, 3.95. $C_{104}H_{101}B_2N_5O_4P_3Re$ (**5b**) requires C, 69.95; H, 5.70; N, 3.9%. IR (KBr, cm^{-1}): 1730 (sh), 1726 (s), 1699 (s) ν(NO). ^{1}H-NMR (CD_2Cl_2-d_2, 25 °C, δ): 12.83, 12.69 (d, NH), 3.52 (m, CH_2), 2.45, 2.42 (s, CH_3), 1.07, 0.97 (t, CH_3 phos) ppm. ^{31}P{^{1}H}-NMR (CD_2Cl_2-d_2, 25 °C, δ): AB_2 spin system, δ_A 104.7 ppm, δ_B 4.58 ppm, $J_{AB} = 24.7$ Hz; AB_2 spin system, δ_A 104.4 ppm, δ_B 4.08 ppm, $J_{AB} = 24.7$ Hz; AB_2 spin system, δ_A 99.9 ppm, δ_B −0.17 ppm, $J_{AB} = 23.7$ Hz. Found: C, 70.95; H, 5.6; N, 4.0. $C_{106}H_{97}B_2N_5O_3P_3Re$ (**6a**) requires C, 71.15; H, 5.5; N, 3.9%. Found: C, 71.4; H, 5.65; N, 3.9. $C_{108}H_{101}B_2N_5O_3P_3Re$ (**6b**) requires C, 71.3; H, 5.60; N, 3.85%. IR (KBr, cm^{-1}): 1716 (s, br) ν(NO). ^{1}H-NMR (CD_2Cl_2-d_2, 25 °C, δ): 12.88, 12.73 (d, NH), 3.63, 3.35 (qnt, CH_2), 2.39, 2.34 (s, CH_3), 1.16, 0.99 (t, CH_3 phos) ppm. ^{31}P{^{1}H}-NMR (CD_2Cl_2-d_2, 25 °C, δ): AB_2 spin system, δ_A 127.3 ppm, δ_B 3.52 ppm, $J_{AB} = 20.0$ Hz; AB_2 spin system, δ_A 122.0 ppm, δ_B −2.0 ppm, $J_{AB} = 19.5$ Hz; AB_2 spin system, δ_A 127.9 ppm, δ_B 3.04 ppm, $J_{AB} = 20.0$ Hz).

2.2.6. *[Re(C_6H_5N=^{15}NH)$_2$(NO)L(PPh_3)$_2$](BPh_4)$_2$ (**5a**$_1$ and **6a**$_1$) [L = P(OEt)$_3$ (**5**), PPh(OEt)$_2$ (**6**)]*

These complexes were prepared exactly like the related unlabelled compounds **5a** and **6a** using $[C_6H_5N{\equiv}^{15}N]BF_4$ as a reagent; yield = 60%.

2.2.7. *[{Re(4-$CH_3C_6H_4N$=NH)(NO)[P(OEt)$_3$](PPh_3)$_2$}$_2$(μ-4,4′-HN=NC_6H_4–C_6H_4N=NH)](BPh_4)$_4$ (**7**)*

In a 25-cm^3 three-necked round-bottomed flask were placed 0.100 g (0.11 mmol) of $ReH_2(NO)\{P(OEt)_3\}(PPh_3)_2$ and 21 mg (0.055 mmol) of $[4,4'\text{-}N_2C_6H_4–C_6H_4N_2](BF_4)_2$. The flask was cooled to −196 °C and 8 cm^3 of CH_2Cl_2 was added. The reaction mixture was brought to 0 °C, stirred for 4 h and then transferred, by cannule, into a 25-cm^3 three-necked flask cooled to −196 °C and containing an excess of solid $[4\text{-}CH_3C_6H_4N_2]BF_4$ (0.32 mmol, 66 mg) diazonium salt. The resulting reaction mixture was brought to −10 °C and stirred for about 6 h. The solvent was removed under reduced pressure, giving an oil which was triturated with ethanol containing an excess of $NaBPh_4$ (0.4 mmol, 0.137 g). A reddish-brown solid slowly separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield = 60%; $\Lambda_M = 284$ S cm^2 mol^{-1}. Found: C, 70.15; H, 5.7; N, 4.1. $C_{206}H_{196}B_4N_{10}O_8P_6Re_2$ requires C, 69.9; H, 5.6; N, 3.95%.

2.2.8. *[ReH(ArN=NH)(NO)(PPh_3)$_3$]BPh_4 (**8**) [Ar = C_6H_5 (**a**), 4-$CH_3C_6H_4$ (**b**)]*

In a 25-cm^3 three-necked round-bottomed flask were placed 0.1 g (0.1 mmol) of $ReH_2(NO)(PPh_3)_3$ and an equimolar amount (0.1 mmol) of the appropriate aryldiazonium tetrafluoborate $[ArN_2]BF_4$ and the flask was cooled to −196 °C. Dichloromethane (10 cm^3) was added and the reaction mixture, brought to 0 °C, was stirred for 50 min. The solvent was removed under reduced pressure to give a brown solid, which was treated with ethanol (5 cm^3). The addition of an excess of $NaBPh_4$ (0.2 mmol, 68 mg) to the resulting solution caused the separation of a reddish-brown solid, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield = 75%; Λ_M (S cm^2 mol^{-1}) = 61.3 for **8a**, 58.6 for **8b**. Found: C, 70.8; H, 5.20; N, 3.0. $C_{84}H_{72}BN_3OP_3Re$ (**8a**) requires C, 70.6; H, 5.1; N, 2.95%. Found: C, 70.8; H, 5.3; N, 3.05. $C_{85}H_{74}BN_3OP_3Re$ (**8b**) requires C, 70.7; H, 5.15; N, 2.9%. IR (KBr, cm^{-1}): 1844 (m) ν(ReH), 1686 (s) ν(NO). ^{1}H-NMR (CD_2Cl_2-d_2, 25 °C, δ): 12.50 (d, J_{PH} = 10 Hz), 12.25 (br) (NH), A_2BX spin system, δ_X 3.65 ppm, $J_{AX} = J_{BX}$ = 7 Hz; A_2BX spin system, δ_X 3.30 ppm, J_{AX} = 15 Hz, J_{BX} = 35 Hz (ReH), 2.33, 2.31 (s, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2-d_2, 25 °C, δ): A_2B spin system, δ_A 16.5 ppm, δ_B 11.0 ppm, J_{AB} = 14.0 Hz; A_2B spin system, δ_A 21.6 ppm, δ_B 14.2 ppm, J_{AB} = 6.3 Hz.

2.2.9. *$[ReH(C_6H_5N{=}^{15}NH)(NO)(PPh_3)_3]BPh_4$ (**8a$_1$**) and $[ReH(C_6H_5^{15}N{=}NH)(NO)(PPh_3)_3]BPh_4$ (**8a$_2$**)*

These complexes were prepared exactly like the related unlabelled compound **8a** using the labelled $[C_6H_5N{\equiv}^{15}N]BF_4$ and $[C_6H_5^{15}N{\equiv}N]BF_4$, respectively, aryldiazonium salts; yield = 65%. For **8a$_1$**: IR (KBr, cm^{-1}): 1844 (w) ν(ReH), 1684 (s) ν(NO). ^{1}H-NMR (CD_2Cl_2-d_2, 25 °C, δ): 12.69 (dd, $^1J_{^{15}NH}$ = 63 Hz, J_{PH} = 10 Hz), 11.46 (d, $J_{^{15}NH}$ = 61 Hz) (NH), A_2BX spin system, δ_X 3.66 ppm, $J_{AX} = J_{BX}$ = 6.9 Hz; A_2BX spin system, δ_X 3.38 ppm, J_{AX} = 34.6 Hz, J_{BX} = 15.6 Hz (ReH). $^{31}P\{^1H\}$-NMR (CD_2Cl_2-d_2, 25 °C, δ): A_2BY spin system, δ_A 16.2 ppm, δ_B 10.8 ppm, J_{AB} = 14.1 Hz, J_{AY} = 1.9 Hz, J_{BY} = 28.1 Hz; A_2BY spin system, δ_A 21.9 ppm, δ_B 14.4 ppm, J_{AB} = 6.3 Hz, J_{AY} = 4.3 Hz, J_{BY} = 2.3 Hz. For **8a$_2$**: IR (KBr, cm^{-1}): 1844 (w) ν(ReH), 1684 (s) ν(NO). ^{1}H-NMR (CD_2Cl_2-d_2, 25 °C, δ): 12.69 (d, br, $^2J_{^{15}NH}$ = 2.5 Hz), 11.47 (br) (NH), A_2BX spin system, δ_X 3.66 ppm, $J_{AX} = J_{BX}$ = 6.9 Hz; A_2BX spin system, δ_X 3.38 ppm, J_{AX} = 34.6 Hz, J_{BX} = 15.6 Hz (ReH). $^{31}P\{^1H\}$-NMR (CD_2Cl_2-d_2, 25 °C, δ): A_2BY spin system, δ_A 16.2 ppm, δ_B 10.8 ppm, J_{AB} = 14.1 Hz, $J_{AY} = J_{BY}$ = < 1 Hz; A_2BY spin system, δ_A 21.9 ppm, δ_B 14.5 ppm, J_{AB} = 6.3 Hz, J_{AY} = 3.3 Hz, J_{BY} = 5.4 Hz.

2.2.10. *$[\{ReH(NO)(PPh_3)_3\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)](BPh_4)_2$ (**9**) [Ar–Ar = 4,4′-C_6H_4–C_6H_4 (**c**), 4,4′-C_6H_4–CH_2–C_6H_4 (**d**)]*

Solid samples of $RuH_2(NO)(PPh_3)_3$ (0.1 g, 0.1 mmol) and the appropriate aryldiazonium tetrafluoborate $[N_2Ar{-}ArN_2](BF_4)_2$ (0.05 mmol) were placed in a 25-cm^3 three-necked round-bottomed flask. The flask was cooled to −196 °C and CH_2Cl_2 (10 cm^3) added. The reaction mixture was brought to 0 °C, stirred for 4 h and then the solvent removed under reduced pressure. The oil obtained was triturated with ethanol containing an excess of $NaBPh_4$ (0.2 mmol, 68 mg). A reddish-brown solid separated out from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield = 70%. Λ_M (S cm^2 mol^{-1}) = 125.1 for **9c**, 138.5 for **9d**. Found: C, 70.7; H, 5.1; N, 3.0. $C_{168}H_{142}B_2N_6O_2P_6Re_2$ (**9c**) requires C, 70.6; H, 5.0; N, 2.95%. Found: C, 70.8; H, 5.15; N, 3.1. $C_{169}H_{144}B_2N_6O_2P_6Re_2$ (**9d**) requires C, 70.70; H, 5.05; N, 2.95%. IR (KBr, cm^{-1}): 1830 (w) ν(ReH), 1684 (s) ν(NO). ^{1}H-NMR (CD_2Cl_2-d_2, 25 °C, δ): 12.55, 11.35 (s, br, NH), A_2BX spin system, δ_X 3.37 ppm, $J_{AX} = J_{BX}$ = 6.86 Hz; A_2BX spin system, δ_X 3.67 ppm, J_{AX} = 34.6 Hz, J_{BX} = 15.6 Hz (ReH). $^{31}P\{^1H\}$-NMR (CD_2Cl_2-d_2, 25 °C, δ): A_2B spin system, δ_A 21.9 ppm, δ_B 14.5 ppm, J_{AB} = 5.8 Hz; A_2B spin system, δ_A 16.3 ppm, δ_B 10.8 ppm, J_{AB} = 13.8 Hz.

2.2.11. *$[\{ReH(NO)(PPh_3)_3\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4{-}C_6H_4N{=}^{15}NH)](BPh_4)_2$ (**9c$_1$**)*

This complex was prepared exactly like the related unlabelled compound **9c** using the $[4,4'\text{-}^{15}N{\equiv}NC_6H_4{-}C_6H_4N{\equiv}^{15}N](BF_4)_2$ bis(aryldiazonium) salt; yield = 60%. IR (KBr, cm^{-1}): 1842 (w) ν(ReH), 1684 (s) ν(NO). ^{1}H-NMR (CD_2Cl_2-d_2, 25 °C, δ): 12.71 (dd, $^1J_{^{15}NH}$ = 66 Hz), 11.5 (d, br, $^1J_{^{15}NH}$ = 63 Hz) (NH), A_2BX spin system, δ_X 3.67 ppm, $J_{AX} = J_{BX}$ = 8 Hz, 3.4 (m) (ReH). $^{31}P\{^1H\}$-NMR (CD_2Cl_2-d_2, 25 °C, δ): A_2BY spin system, δ_A 16.2 ppm, δ_B 10.9 ppm, J_{AB} = 14.0 Hz, J_{AY} = 1.8 Hz, J_{BY} = 28.5 Hz; A_2BY spin system, δ_A 22.1 ppm, δ_B 14.6 ppm, J_{AB} = 6.3 Hz, J_{AY} = 22.9 Hz, J_{BY} = 17.2 Hz.

2.2.12. *$[ReH(C_6H_5N_2)\{PPh(OEt)_2\}_4]BPh_4$ (**11a**)*

Solid samples of $ReH_3\{PPh(OEt)_2\}_4$ (0.100 g, 0.102 mmol) and of an excess of $[C_6H_5N_2]BF_4$ (0.77 mg, 0.4 mmol) were placed in a 25-cm^3 three-necked round-bottomed flask and cooled to −196 °C. Dichloromethane (8 cm^3) was added and the reaction mixture, brought to 0 °C, was stirred for 2 h at this temperature and then for other 4 h at about 22 °C. The solvent was removed under reduced pressure giving an oil which was treated with ethanol containing an excess of $NaBPh_4$ (0.14 g, 0.4 mmol). A reddish-brown solid slowly separated out from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield = 30%; Λ_M = 62.7 S cm^2 mol^{-1}. Found: C, 60.1; H, 6.3; N, 2.0. $C_{70}H_{86}BN_2O_8P_4Re$ requires C, 59.9; H, 6.15; N, 2.0%.

2.2.13. *[ReH($C_6H_5N{\equiv}^{15}N$){PPh(OEt)$_2$}$_4$]BPh$_4$* (*11a$_1$*)

This complex was prepared following the method reported for the related unlabelled compound **11a** using $[C_6H_5N{\equiv}^{15}N]BF_4$ as a reagent; yield $=30\%$.

3. Results and discussion

3.1. Preparation of hydride complexes

The synthesis of bis(aryldiazene) complexes of rhenium was achieved using the new $ReH_2(NO)L(PPh_3)_2$ [$L=P(OEt)_3$ and $PPh(OEt)_2$] mixed-ligand hydrides as precursors. The preparation of these mixed-ligand hydrides deserves some further comments. Treatment of $ReH_2(NO)(PPh_3)_3$ with an excess of phosphites gives the $ReH_2(NO)L(PPh_3)_2$ derivatives, which were isolated and characterised (Scheme 1).

The reaction proceeds with the replacement of only one PPh_3 and with the exclusive formation of the mixed-ligand $ReH_2(NO)L(PPh_3)_2$ compounds. They are pale-yellow solids stable in air and in a solution of common organic solvents, where they behave as non-electrolytes. Analytical and spectroscopic data (Table 1) support the proposed formulation.

The infrared spectrum of each of the two hydride compounds shows one strong absorption at 1607 cm^{-1}, due to the ν(NO), and one medium-intensity slightly broad band at 1823 and 1844 cm^{-1}, attributed to the stretching of the Re–H bond.

The proton NMR spectra confirm the presence of the hydride ligands, showing a complicated multiplet between -0.46 and -3.46 ppm. Taking into account that the $^{31}P\{^1H\}$-NMR spectra display a AB_2 multiplet, the hydride pattern can be simulated using an AB_2XY model (with $X=H_A$ and $Y=H_B$) whose parameters are reported in Table 1.

$$ReH_2(NO)(PPh_3)_3 \xrightarrow[\text{reflux}]{\text{exc. L}} ReH_2(NO)L(PPh_3)_2$$

Scheme 1. $L=P(OEt)_3$ and $PPh(OEt)_2$.

$$ReH_2(NO)L(PPh_3)_2 + ArN_2^+ \xrightarrow{CH_2Cl_2} \underset{\mathbf{1,\,2}}{[ReH(ArN{=}NH)(NO)L(PPh_3)_2]^+} \longrightarrow$$

$$\xrightarrow[CH_2Cl_2]{\text{exc. }ArN_2^+} \underset{\mathbf{5,\,6}}{[Re(ArN{=}NH)_2(NO)L(PPh_3)_2]^{2+}}$$

Scheme 2. $Ar=C_6H_5$ (**a**), 4-$CH_3C_6H_4$ (**b**); $L=P(OEt)_3$ (**1** and **5**), $PPh(OEt)_2$ (**2** and **6**).

On the basis of these data, a geometry of type **I** (Fig. 1), with the two hydride ligands in a mutually *cis* position, can reasonably be proposed for the $ReH_2(NO)L(PPh_3)_2$ mixed-ligand derivatives.

3.2. Aryldiazene derivatives

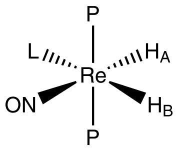
The synthesis of bis(aryldiazene) complexes of rhenium $[Re(ArN{=}NH)_2(NO)L(PPh_3)_2](BPh_4)_2$ (**5** and **6**) was achieved by reacting the $ReH_2(NO)L(PPh_3)_2$ mixed-ligand hydrides with an excess of aryldiazonium cations in CH_2Cl_2, as shown in Scheme 2.

Studies on the reaction course revealed that the treatment of $ReH_2(NO)L(PPh_3)_2$ hydrides with an equimolar amount of ArN_2^+ gives the $[ReH(ArN{=}NH)(NO)L(PPh_3)_2]^+$ monodiazene cations **1** and **2**, which further react with an excess of aryldiazonium salt to give the final bis(aryldiazene) derivatives **5** and **6**.

Bis(aryldiazonium) cations $[N_2Ar{-}ArN_2]^{2+}$ also react with $ReH_2(NO)L(PPh_3)_2$ dihydrides in a 1:2 ratio to give binuclear complexes **3** and **4** with a di-diazene bridging unit (Scheme 3).

These binuclear complexes **3** and **4** were treated with an excess of monodiazonium ArN_2^+ cation in order to test whether further insertion on the Re–H bond can take place to give bis(aryldiazene) species. In only one case does the reaction proceed to give the binuclear complex **7**, which was isolated in pure form and characterised (Scheme 4).

It is important to note that only the $ReH_2(NO)L(PPh_3)_2$ dihydride, containing mixed phosphite–phosphine ligands, undergoes insertion of two ArN_2^+ groups into the two Re–H bonds, yielding bis(aryldiazene) complexes. The related triphenylpho-



I

Fig. 1.

$$[\{ReH(NO)L(PPh_3)_2\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{2+} \xrightarrow[CH_2Cl_2]{\text{exc. }ArN_2^+}$$

$$\longrightarrow \underset{\mathbf{7}}{[\{Re(ArN{=}NH)(NO)L(PPh_3)_2\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{4+}}$$

Scheme 4. $Ar=4\text{-}CH_3C_6H_4$; $Ar{-}Ar=4,4'\text{-}C_6H_4{-}C_6H_4$; $L=P(OEt)_3$.

$$2ReH_2(NO)L(PPh_3)_2 + [N_2Ar{-}ArN_2]^{2+} \longrightarrow \underset{\mathbf{3,\,4}}{[\{ReH(NO)L(PPh_3)_2\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{2+}}$$

Scheme 3. $Ar{-}Ar=4,4'\text{-}C_6H_4{-}C_6H_4$ (**c**), $4,4'\text{-}C_6H_4{-}CH_2{-}C_6H_4$ (**d**); $L=P(OEt)_3$ (**3**), $PPh(OEt)_2$ (**4**).

Table 1
IR and NMR data for selected rhenium complexes

	Compound	IR [a] ν (cm^{-1})	Assgnt	^{1}H-NMR [b,c] δ (J, Hz)	Assgnt	Spin system	^{31}P{^{1}H}-NMR [b,d] δ (J, Hz)
	$ReH_2(NO)\{PPh(OEt)_2\}(PPh_3)_2$	1823w,-br, 1607s	ν(ReH), ν(NO)	3.68 (m) [e], 3.46 (m), 0.88 (t), AB_2XY spin syst, δ_X −0.46, δ_Y −3.07, $J_{AX} = 39.6$, $J_{AY} = 53.3$, $J_{BX} = 29.3$, $J_{BY} = 20.5$, $J_{XY} = 5.4$	CH_2, CH_3, ReH	AB_2 [e]	δ_A 150.8, δ_B 26.6, $J_{AB} = 10.4$
	$ReH_2(NO)\{P(OEt)_3\}(PPh_3)_2$	1844m, 1607s	ν(ReH), ν(NO)	3.54 (qnt), 0.84 (t), AB_2XY spin syst, δ_X −0.48, δ_Y −3.46, $J_{AX} = 52.8$, $J_{AY} = 54.4$, $J_{BX} = 29.3$, $J_{BY} = 21.5$, $J_{XY} = 5.0$	CH_2, CH_3, ReH	AB_2	δ_A 140.9, δ_B 26.6, $J_{AB} = 13.5$
1a	$[ReH(C_6H_5N{=}NH)(NO)\{P(OEt)_3\}(PPh_3)_2]BPh_4$	1885w, 1701s	ν(ReH), ν(NO)	12.96 (d, br), $^{3}J_{PH} = 6$, 11.60 (d, br), $^{3}J_{PH} = 6$, 4.10 (m), 3.51 (qnt), 3.48 (qnt), 1.05 (t), 0.92 (t)	NH, ReH, CH_2, CH_3	AB_2, AB_2	δ_A 113.6, δ_B 24.1, $J_{AB} = 12.9$, δ_A 107.2, δ_B 18.2, $J_{AB} = 23.7$
1a$_1$	$[ReH(C_6H_5N{=}^{15}NH)(NO)\{P(OEt)_3\}(PPh_3)_2]BPh_4$	1886w, 1701s	ν(ReH), ν(NO)	12.95 (dm), $^{1}J_{15_{NH}} = 64$, 11.60 (dm), $^{1}J_{15_{NH}} = 64$, 4.10 m, 3.48 (qnt), 3.51 (qnt), 1.05 (t), 0.92 (t)	NH, ReH, CH_2, CH_3	AB_2Y, AB_2Y	δ_A 113.6, δ_B 24.0, $J_{AB} = 12.9$, $J_{AY} = 5.0$, $J_{BY} = 4.3$, δ_A 107.2, δ_B 18.2, $J_{AB} = 23.7$, $J_{AY} = 40.9$, $J_{BY} = 2.9$
4c	$[\{ReH(NO)\{PPh(OEt)_2\}(PPh_3)_2\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_2$ [f]	1816w, 1684s	ν(ReH), ν(NO)	13.10 (d, br), 11.4 (s, br), 3.69 (m), 3.15 (m), 1.02 (t), 0.83 (t)	NH, CH_2, CH_3	AB_2, AB_2	δ_A 125.0, δ_B 11.4, $J_{AB} = 18.1$, δ_A 131.6, δ_B 18.4, $J_{AB} = 9.6$
5a	$[Re(C_6H_5N{=}NH)_2(NO)\{P(OEt)_3\}(PPh_3)_2](BPh_4)_2$	1730sh, 1717s, 1701s	ν(NO)	13.00 (d), 12.89 (d), 3.61 (qnt), 3.55 (qnt), 1.06 (t), 0.95 (t)	NH, CH_2, CH_3	AB_2, AB_2, AB_2	δ_A 99.6, δ_B −0.46, $J_{AB} = 24.4$, δ_A 104.4, δ_B 4.43, $J_{AB} = 23.8$, δ_A 104.1, δ_B 3.95, $J_{AB} = 24.5$
5a$_1$	$[Re(C_6H_5N{=}^{15}NH)_2(NO)\{P(OEt)_3\}(PPh_3)_2](BPh_4)_2$	1730sh, 1718s, 1701sh	ν(NO)	13.01 (dd), $^{1}J_{15_{NH}} = 64$, 12.88 (dd), $^{1}J_{15_{NH}} = 64$, 3.60 (qnt), 3.54 (qnt), 1.06 (t), 0.95 (t)	NH, CH_2, CH_3	AB_2Y_2, AB_2Y_2, AB_2Y_2	δ_A 99.6, δ_B −0.46, $J_{AB} = 24.4$, $J_{AY} = 55.4$, $J_{BY} = 0.1$, δ_A 104.0, δ_B 3.95, $J_{AB} = 24.4$, $J_{AY} = 28.6$, $J_{BY} = 0.1$, δ_A 104.4, δ_B 4.45, $J_{AB} = 23.8$, $J_{AY} = 27.9$, $J_{BY} = 0.1$
6a	$[Re(C_6H_5N{=}NH)_2(NO)\{PPh(OEt)_2\}(PPh_3)_2](BPh_4)_2$	1730s, 1720s, 1701sh	ν(NO)	13.06 (d), 3.46 (qnt), 3.32 (qnt), 0.93 (t)	NH, CH_2, CH_3	AB_2, AB_2	δ_A 126.9, δ_B 3.34, $J_{AB} = 20.3$, δ_A 127.1, δ_B 2.88, $J_{AB} = 19.4$
6a$_1$	$[Re(C_6H_5N{=}^{15}NH)_2(NO)\{PPh(OEt)_2\}(PPh_3)_2](BPh_4)_2$ [g]	1730s, 1701sh	ν(NO)	13.05 (dd), $^{1}J_{15_{NH}} = 62$, 12.90 (dd), $^{1}J_{15_{NH}} = 64$, 3.60 (qnt), 3.45 (qnt), 3.33 (qnt), 1.13 (t), 0.93 (t)	NH, CH_2, CH_3	AB_2Y_2, AB_2Y_2, AB_2Y_2	δ_A 127.2, δ_B 2.90, $J_{AB} = 19.4$, $J_{AY} = 28.7$, $J_{BY} = 1.0$, δ_A 126.9, δ_B 3.34, $J_{AB} = 20.3$, $J_{AY} = 28.1$, $J_{BY} = 1.0$, δ_A 121.9, δ_B −2.0, $J_{AB} = 19.8$, $J_{AY} = 48.7$, $J_{BY} = 1.0$
7	$[\{Re(4\text{-}CH_3C_6H_4N{=}NH)(NO)\{P(OEt)_3\}(PPh_3)_2\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_4$	1718s,br	ν(NO)	12.9 (m), 3.52 (m), 2.44 (s), 2.40 (s), 1.06 (t), 0.95 (t)	NH, CH_2, CH_3, CH_3 phos	AB_2, AB_2,AB_2	δ_A 99.4, δ_B −0.29, $J_{AB} = 26.0$, δ_A 104.1, δ_B 4.52, $J_{AB} = 20.0$, δ_A 103.8, δ_B 4.08, $J_{AB} = 25.0$
8a	$[ReH(C_6H_5N{=}NH)(NO)(PPh_3)_3]BPh_4$	1844m, 1684s	ν(ReH), ν(NO)	12.69 (d), $J_{PH} = 10$, 11.46 (br), A_2BX spin syst, δ_X 3.66, $J_{AX} = J_{BX} = 6.9$, A_2BX spin syst, δ_X 3.38, $J_{AX} = 34.6$, $J_{BX} = 15.6$	NH, ReH	A_2B, A_2B	δ_A 16.2, δ_B 10.8, $J_{AB} = 14.0$, δ_A 21.9, δ_B 14.5, $J_{AB} = 6.3$
9c	$[\{ReH(NO)(PPh_3)_3\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_2$	1842w, 1684s	ν(ReH), ν(NO)	12.72 (d, br), 11.50 (s, br), A_2BX spin syst, δ_X 3.67, $J_{AX} = J_{BX} = 8$, 3.40 (m)	NH, ReH	A_2B, A_2B	δ_A 16.1, δ_B 10.7, $J_{AB} = 14.0$, δ_A 22.1, δ_B 14.6, $J_{AB} = 6.3$

Table 1 (*Continued*)

	Compound	IR [a] ν (cm^{-1})	Assgnt	^{1}H-NMR [b,c] δ (J, Hz)	Assgnt	Spin system	^{31}P{^{1}H}-NMR [b,d] δ (J, Hz)
11a	$[ReH(C_6H_5N_2)\{PPh(OEt)_2\}_4]BPh_4$	1680m	$\nu(N\equiv N)$	3.62 (qnt), 1.20 (t), −4.51 (qnt), $^2J_{PH} = 18$	CH$_2$, CH$_3$, ReH	A_4	117.5 (s)
11a$_1$	$[ReH(C_6H_5N\equiv{}^{15}N)\{PPh(OEt)_2\}_4]BPh_4$	1653m	$\nu(^{15}N\equiv N)$	3.63 (qnt), 1.20 (t), −4.51 (qnt), $^2J_{PH} = 18$	CH$_2$, CH$_3$, ReH	A_4Y	117.5 (d), $J_{AY} = 5.2$

[a] In KBr pellets.

[b] In CD_2Cl_2 at 25 °C, unless otherwise noted.

[c] Phenyl proton resonances are omitted.

[d] Positive shift downfield from 85% H_3PO_4.

[e] In C_6D_6.

[f] In $CDCl_2CDCl_2$.

[g] ^{15}N-NMR (CD_2Cl_2, 25 °C) δ: −3.6 (dt, $^2J_{^{31}P^{15}N} = 28.3$ Hz, $^2J_{^{31}P^{15}N} = 1.0$ Hz), −4.3 (dt, $^2J_{^{31}P^{15}N} = 28.3$ Hz, $^2J_{^{31}P^{15}N} = 1.0$ Hz), −8.6 (dt, $^2J_{^{31}P^{15}N} = 48.5$ Hz, $^2J_{^{31}P^{15}N} = 1.0$ Hz).

sphine $ReH_2(NO)(PPh_3)_3$ compound, as well as the tris(phosphite) $ReH_2(NO)(PPh_2OEt)_3$ derivative [11], instead, react with aryldiazonium cations yielding rather the monoaryldiazene complexes, which can be isolated and characterised (Scheme 5).

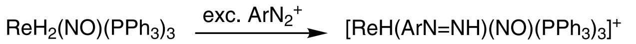
Also binuclear $[\{ReH(NO)(PPh_3)_2\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)]^{2+}$ complexes **9** can be prepared by reacting $ReH_2(NO)(PPh_3)_3$ with a bis(aryldiazonium) salt in a 1:2 ratio (Scheme 6).

All the aryldiazene complexes **1**–**9** were isolated as yellow or orange solids stable in air and in a solution of polar organic solvents, in which they behaved as 1:1 (**1**, **2**, **8**), 2:1 (**3**, **4**, **5**, **6**, **9**) and 4:1 (**7**) electrolytes [12]. The analytical and spectroscopic data, reported in Table 1, support the proposed formulations. Furthermore, the NMR spectra also show that the complexes were often obtained as a mixture of two or more isomers that we were not able to separate. Fractional crystallisation, for example, gave only solid samples enriched in one isomer, whereas the chromatography on silica gel or alumina caused the decomposition of the complexes.

The IR spectra of monodiazene **1** and **2** complexes showed a strong band in the ν(NO) region at 1701–1674 cm^{-1} due to the nitrosyl ligand and a medium-intensity absorption at 1885–1871 cm^{-1} attributed to the stretching of the Re–H bond. The width of these bands, however, does not allow us to emphasise the presence of more isomers.

The ^{1}H-NMR spectra of $[ReH(ArN{=}NH)(NO)L(PPh_3)_2]^+$ (**1** and **2**) cations, instead, show two NH signals between 13.08 and 11.2 ppm, each of which are split into two doublets in the labelled **1a**$_1$ and **2a**$_1$ compounds, with $^1J_{NH}$ values of 61–64 Hz, in agreement with the presence of two species containing the diazene ligand [1,13]. Besides the signals of the phosphines and BPh_4^- anions, the resonances of the hydride ligands are also present in the spectra, which appear between 4.10 and 3.65 ppm as two well-separated multiplets in some case or as two overlapping signals in others. These resonances fall in an unusual region for hydride ligands [14], probably owing to the presence of the nitrosyl group in the cationic complexes. However, heterodecoupling experiments emphasise the characteristic coupling of the hydride with the phosphorus nuclei of the phosphine thus confirming the assignment. Furthermore, taking into account that the ^{31}P{^{1}H}-NMR spectra of **1** and **2** show two well-separated AB_2 multiplets, the two hydride patterns at 5–3 ppm may also be simulated, in the case of both **2a** and **2b**, using two AB_2X models (X = H), with the parameters reported in Table 1.

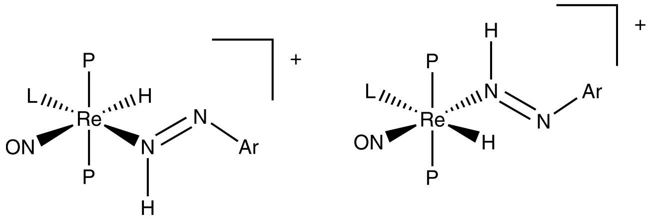
The presence of two signals for the hydride, of two NH resonances and of two ^{31}P multiplets, suggests the existence of two isomers for complexes **1** and **2**, which are probably formed by the insertion of the ArN_2^+ group into the two non-equivalent Re–H bonds of the



$$\mathrm{ReH_2(NO)(PPh_3)_3} \xrightarrow[\mathrm{CH_2Cl_2}]{\text{exc. } \mathrm{ArN_2^+}} \mathrm{[ReH(ArN{=}NH)(NO)(PPh_3)_3]^+}$$

8

Scheme 5. Ar = C_6H_5 (**a**), 4-$CH_3C_6H_4$ (**b**).



II **III**

Fig. 2.

$ReH_2(NO)L(PPh_3)_2$ precursors. Both hydrides are probably reactive toward the insertion of the aryldiazonium cation. The reaction of only one of the ArN_2^+ should give rise to two different species with geometries of type **II** and **III** of Fig. 2 as for example. In order to establish that the geometry in solution of the two isomers are really **II** and **III**, it is useful to examine the value of the J_{PH} between the hydride and phosphorus nuclei, and the value $J_{^{31}\mathrm{P}^{15}\mathrm{N}}$ between the diazene and the phosphine in the labelled **1a**$_1$ and **2a**$_1$ complexes (Table 1).

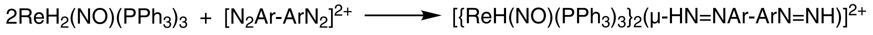
In the case of **2b**, the results showed that in one isomer (**II**) the two J_{PH} have similar values, while in the other (**III**) one of the J_{PH} is higher than the other, suggesting the mutually *trans* position of the hydride and of one of the phosphines. Also in one isomer (**II**), the diazene ligand is *trans* to one phosphine. This can be deduced by the higher $J_{^{31}\mathrm{P}^{15}\mathrm{N}}$ value of 40.9 or 34.4 Hz observed in one multiplet of the ^{31}P spectra of the labelled **1a**$_1$ and **2a**$_1$ complexes. It is therefore reasonable to propose the **II** and **III** geometries for the two isomers present in our mononuclear monodiazene $[ReH(ArN{=}NH)(NO)L(PPh_3)_2]BPh_4$ (**1** and **2**) derivatives.

Also in the related binuclear $[\{ReH(NO)L(PPh_3)_2\}_2(\mu\text{-}HN{=}NAr\text{–}ArN{=}NH)](BPh_4)_2$ (**3** and **4**) complexes, the infrared spectra confirm the presence of both the nitrosyl and the hydride ligands, showing the $\nu(NO)$ at 1684–1695 cm^{-1} and the $\nu(Re\text{–}H)$ at 1890–1816 cm^{-1}. The ^1H-NMR spectra show the characteristic signals of the diazene ligand in the high-frequency region, which are seen as two well-separated broad signals, suggesting the presence of two isomers in this case as well. This is also confirmed by the $^{31}P\{^1H\}$ spectra, which show two well-separated multiplets. These multiplets are, however, slightly broad, and their simulation using a AB_2 model is, in the case of complex **4c**, rather difficult, because the spectra seem to contain several overlapping systems. The results may be explained on the basis of a restricted rotation of the phosphorus ligand around the Re–P bond, affording more isomers with inequivalent phosphorus nuclei [15]. In order to test this hypothesis, we have registered the ^{31}P spectra between +50 and −80 °C and observed no significant variation in the spectra whose broad multiplets do not resolve with the changing temperature. We have then used a different solvent and observed that with $CDCl_2CDCl_2$, two well-resolved AB_2 multiplets appear in the spectra of **4c**, which were easily simulated with parameters reported in Table 1. These results show that the nature of the solvent or rather the interaction of our rhenium cations with the solvent are important in determining the ^{31}P-NMR spectra resolution.

The infrared and NMR data, however, do not allow a precise determination of the geometry in solution for the two isomers present in the binuclear **3** and **4** complexes. This is due to the nature of the hydride signals, which in part overlap with the methylene multiplet thus preventing the determination of the J_{PH} value. It can also be noted that the reaction of $ReH_2(NO)L(PPh_3)_2$ with bis(aryldiazonium) salts should give four isomers of type **II**–**II**, **III**–**III**, **II**–**III** and **III**–**II** (see Fig. 2) by analogy with the monodiazonium species **1** and **2**. These are formed with different rates due to the different reactivities towards $[N_2Ar\text{–}ArN_2]^{2+}$ of the two H^- ligands in the $ReH_2(NO)L(PPh_3)_2$ precursor. One of the three isomers is probably formed so slowly to result present only as traces.

Good analytical data were obtained for the bis(aryldiazene) $[Re(ArN{=}NH)_2(NO)L(PPh_3)_2](BPh_4)_2$ (**5** and **6**) complexes, which are orange solids stable in air and in a solution of polar organic solvents, where they behave as 1:2 electrolytes [12]. The IR and NMR data (Table 1) support the proposed formulation and also indicate the presence of more isomers. The IR spectra of complexes **5** and **6**, which contain only one NO ligand, in fact show two or three bands in the $\nu(NO)$ region suggesting the presence of more than one species.

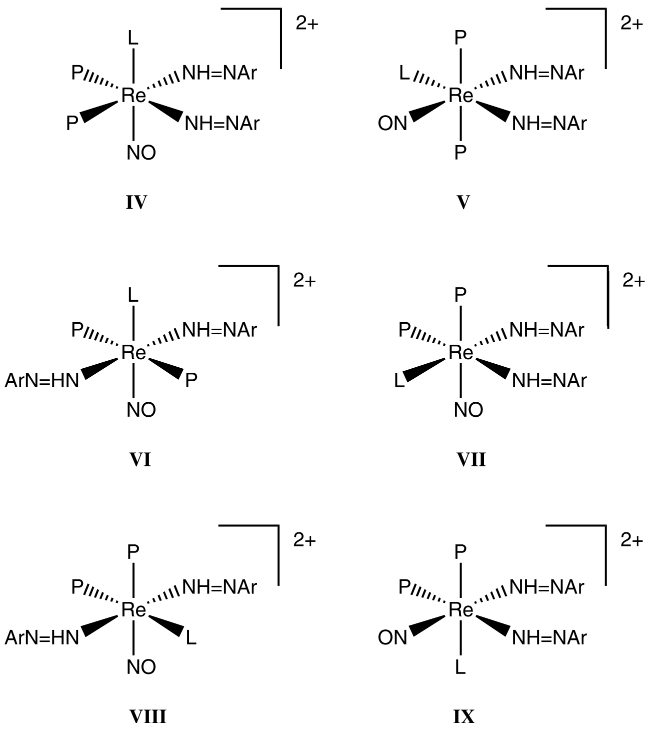
The $^{31}P\{^1H\}$-NMR data confirm the presence of more isomers, showing two or three AB_2 multiplets in the spectra, which can be simulated with the parameters reported in Table 1. The ^1H-NMR spectra also show the presence of one or two doublets in the high-field region attributed to NH resonances of the aryldiazene ligand. Each of these doublets is split into a doublet of doublets in the spectra of the labelled **5a**$_1$ and **6a**$_1$ complexes, with $^1J_{^{15}\mathrm{NH}}$ values of 62–64 Hz, in agreement with the presence of the ArN=NH group [15].



$$\mathrm{2ReH_2(NO)(PPh_3)_3 + [N_2Ar\text{-}ArN_2]^{2+} \longrightarrow [\{ReH(NO)(PPh_3)_3\}_2(\mu\text{-}HN{=}NAr\text{-}ArN{=}NH)]^{2+}}$$

9

Scheme 6. Ar–Ar = 4,4′-C_6H_4–C_6H_4 (**c**), 4,4′-C_6H_4–CH_2–C_6H_4 (**d**).



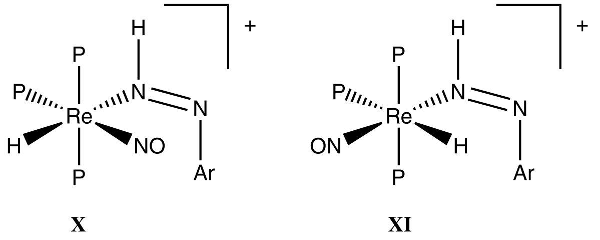
IV V VI VII VIII IX

Fig. 3.

The geometry of the bis(aryldiazene) complexes **5** and **6** can be discussed in terms of the following six structures, reported in Fig. 3.

However, taking into account that all the ^{31}P multiplets observed in the spectra of **5** and **6** are of the AB_2-type, the geometries **VII**, **VIII** and **IX** can be excluded, because and ABC-type ^{31}P spectrum must be expected. Therefore, for the three isomers present in our samples of **5** and **6**, the three **IV**, **V** and **VI** geometries can be reasonably proposed. It can also be noted that the ^1H-NMR signals of the NH groups are less than those expected for the presence of three isomers of **IV**, **V** and **VI** geometries. An overlapping of the NH proton signals is probably present. This is also observed in the $^{15}N\{^1H\}$-NMR spectra of **6a**$_1$, which show three doublets of triplets (Table 1), instead of the four expected.

The analytical and spectroscopic data of the binuclear $[\{Re(4\text{-}CH_3C_6H_4N{=}NH)(NO)\{P(OEt)_3\}(PPh_3)_2\}_2(\mu\text{-}4,4'\text{-}NH{=}NC_6H_4{-}C_6H_4N{=}NH)](BPh_4)_4$ (**7**) compound support its formulation. The diazene proton signals appear as a multiplet at 12.9 ppm, while two methyl groups of the $4\text{-}CH_3C_6H_4N{=}NH$ ligand appear as singlets at 2.40 and 2.44 ppm. The $^{31}P\{^1H\}$-NMR spectra suggest the presence of more isomers in this case as well, showing three AB_2 multiplets which can be simulated using the parameters reported in Table 1. These data, however, do not allow the unambiguous determination of a geometry for the species present in solution of this binuclear derivative.



X XI

Fig. 4.

As reported above, only the mixed-ligand $ReH_2(NO)L(PPh_3)_2$ complexes allow bis(aryldiazene) to be prepared. The related $ReH_2(NO)(PPh_3)_3$ hydride exclusively gives the monoaryldiazene $[ReH(ArN{=}NH)(NO)(PPh_3)_3]BPh_4$ (**8**) complexes, which were isolated and characterised in the usual way by analytical and spectroscopic data (Table 1). The NMR data suggest the presence of two isomers of geometry **X** and **XI** type (Fig. 4) in this case as well. These are formed by the insertion of only one ArN_2^+ group into one of the two hydrides of the $ReH_2(NO)(PPh_3)_3$ precursor. In the temperature range between +30 and −80 °C, the $^{31}P\{^1H\}$-NMR spectra for each compound show, in fact, two A_2B multiplets, while the proton spectra show two NH signals between 12.69 and 11.25 ppm and two hydride multiplets between 3.66 and 3.30 ppm. The simulation of these multiplets using an A_2BX ($X = H$) model allows the J_{PH} values to be calculated (Table 1), and these suggest that in one isomer (**XI**) the hydride is *trans* to one phosphine, while in the other it is in a mutually *cis* position with all the phosphorus nuclei (**X**). Furthermore, the values of the $J_{^{31}P^{15}N}$ determined for compound **8a**$_1$ seem to indicate that the ArN=NH ligand occupies the same position with respect to all the phosphines in both the two isomers, in agreement with the proposed **X** and **XI** geometries for complex **8**.

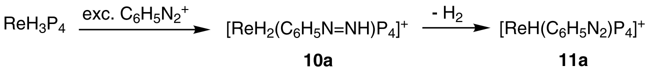
The monodiazene species **8** were treated with ArN_2^+ in an attempt to prepare bis(aryldiazene) complexes, but only mixtures of unstable products were obtained whose NMR spectra do not show the presence of diazenic species.

Only the substitution of one PPh_3 with either $P(OEt)_3$ or $PPh(OEt)_2$ in $ReH_2(NO)(PPh_3)_3$ makes the $[Re(NO)L(PPh_3)_2]$ fragment able to stabilise two aryldiazene ligands bonded to the same central metal.

Binuclear complexes of the $[\{ReH(NO)(PPh_3)_3\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)](BPh_4)_2$ (**9**) type were also prepared from the reaction of $ReH_2(NO)(PPh_3)_3$ with didiazonium $[ArN_2{-}N_2Ar]^{2+}$ salts and their characterisation by NMR data (Table 1) indicate the formation of more isomers in this case as well.

3.3. Aryldiazenido complexes

The results obtained in the reaction of dihydride species $ReH_2(NO)L(PPh_3)_2$ and $ReH_2(NO)(PPh_3)_3$ with



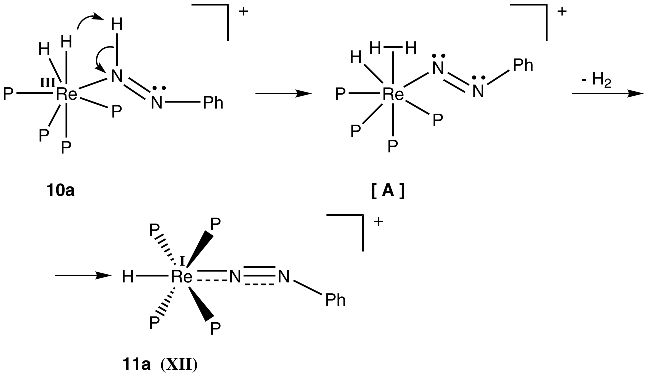
Scheme 7. P = PPh(OEt)$_2$.

ArN_2^+ prompted us to extend the studies to other polyhydrides and the results obtained with the trihydride ReH_3P_4 are reported in Scheme 7.

The ReH_3P_4 hydride reacts with both an equimolar or an excess amount of phenyldiazonium cation to give the aryldiazenido complex **11a** after workup, which was then isolated and characterised. The reaction was also studied by NMR spectroscopy, following the progress of the reaction at variable temperatures in an NMR tube. The spectra indicate that the aryldiazonium cation inserts into only one Re–H bond to give the monodiazene $[ReH_2(C_6H_5N{=}NH)P_4]^+$ (**10a**) cation. This species, however, is rather unstable and cannot be isolated in pure form, but only as a mixture containing **10a** and **11a** and other unidentified compounds. The ^{1}H and ^{31}P spectra, however, strongly support its formulation showing a doublet at 13.95 ppm in the high-frequency region, which is split into one doublet of doublets ($^1J_{15_{NH}} = 62$ Hz) in the spectra obtained using the labelled $C_6H_5N{\equiv}^{15}N^+$ cation, in agreement with the presence of an aryldiazene ligand. In the proton spectra of the reaction mixture, the disappearance of the hydride signal of the precursor ReH_3P_4 at −6.5 ppm and the appearance of a new quintet at −3.96 ppm can also be observed. This signal is split into a doublet of quintets owing to the coupling with ^{15}N when the labelled $[C_6H_5N{\equiv}^{15}N]^+$ cation is used, in agreement with the proposed formulation.

The hydride signal at −3.96 ppm does not change as the temperature is lowered and appears always as a sharp quintet even at −90 °C. Also the slightly broad singlet of the related $^{31}P\{^1H\}$-NMR spectra appears unchanged in the temperature range from +20 to −90 °C, and these results prevent the determination of a geometry in solution of this heptacoordinate complex **10a**. The NMR data, however, strongly support its formulation as an aryldiazene-hydride cation of the $[ReH_2(C_6H_5N{=}NH)P_4]^+$ type. The spectra of the reaction mixture also indicate that no other aryldiazene species, besides **10a**, is formed, even in the presence of an excess of aryldiazonium cation, suggesting that the insertion of only one ArN_2^+ takes place on the phosphite-containing ReH_3P_4 trihydride derivative.

The $[ReH_2(C_6H_5N{=}NH)P_4]^+$ (**10a**) aryldiazene is unstable in solution even at 0 °C and concurrent with this decomposition its ^{1}H-NMR spectrum shows the appearance of a quintet at −4.51 ppm due to the formation of the aryldiazenido $[ReH(C_6H_5N_2)P_4]^+$ (**11a**) derivative. In the spectra, a singlet at 4.6 ppm also appears which decreases on shaking the NMR tube and may be attributed [16] to the signal of free H_2. The presence of dihydrogen in the reaction mixture may suggest the path of Scheme 8 for the formation of the aryldiazenido complex **11a**.



Scheme 8.

The presence of molecular hydrogen in the reaction mixture may be explained by taking the properties of both the diazene and the hydride ligand in the rhenium complexes [1,2,4,6,10,17], into account, i.e. the acidity of the diazene hydrogen atom on one hand and the easy protonation of the hydride ligand on the other, which potentially allow the formation of a η^2-H_2 ligand. Thus, an intramolecular acid–base reaction between the diazene proton of $C_6H_5N{=}NH$ and the Re–H hydride may give rise to a very unstable di-hydrogen intermediate [**A**] which, by the loss of its H_2 and the rearrangement of the ArN_2^- ligand to ArN_2^+ (see below), gives rise to the final aryldiazenido complex **11a**.

The aryldiazenido complex **11a** is a yellow solid, stable in air and in a solution of polar organic solvents, diamagnetic and 1:1 electrolyte. Analytical and spectroscopic data (Table 1) support its formulation. We also attempted to determine the X-ray crystal structure, but the poor quality of the obtained crystals prevented this determination. The IR spectrum shows a medium-intensity band at 1680 cm^{-1}, attributed to the ν(NN) of the $C_6H_5N_2$ ligand. This band shifts to 1653 cm^{-1} in the labelled $[ReH(C_6H_5N{\equiv}^{15}N)P_4]BPh_4$ (**11a**$_1$) complex, according to the proposed assignment. The value for the N–N stretching frequency is indicative of a singly-bent aryldiazenido ligand [6d,18], which should be considered formally present as an ArN_2^+ group. The rhenium central metal must therefore be in a formal oxidation state of +1 [Re(I)], according to geometry **XII** of Scheme 8. In the temperature range between +20 and −80 °C, the $^{31}P\{^1H\}$-NMR spectra of **11a** is a sharp singlet, suggesting the magnetic equivalence of the four phosphite ligands, as expected for a geometry containing the hydride and the ArN_2 ligand in a mutually *trans* position.

Aryldiazenido complexes of rhenium are known [19], but none containing also a hydride ligand as in compound **11a**. We [6d] have previously prepared a related complex of the $[ReCl(PhN_2)\{PPh(OEt)_2\}_4]BPh_4$ type $[\nu(NN) = 1662\ cm^{-1}]$ from the reaction of $ReCl_3P_3$ with hydrazine, but it contained Cl instead of the hydride. The use of the trihydride ReH_3P_4 as a precursor in the reaction with aryldiazonium cations allows the synthesis of hydride-aryldiazenido complex of rhenium to be easily achieved.

The preparation of the aryldiazenido complex **11a** from an aryldiazene prompted us to study the behaviour of the diazene complexes **1**–**9** towards a base, in order to test whether a deprotonation reaction can take place affording new aryldiazenido derivatives. The results show that, whereas the monoaryldiazenes **1**–**4**, **8** and **9** are unreactive towards a base, the bis(aryldiazene) **5** and **6** complexes react with triethylamine in CH_2Cl_2 to give a reddish-brown solution from which, however, no stable aryldiazenido complex was isolated. The deprotonation of both mono- and bis(aryldiazene) complexes **1**–**9**, therefore, does not seem to be the way to obtain aryldiazenido derivatives of rhenium.

3.4. Conclusions

This contribution reports some new results on the chemistry of "diazo" complexes of rhenium containing nitrosyl as a supporting ligand. The first bis(aryldiazene) complexes of rhenium of the $[Re(ArN{=}NH)_2(NO)L(PPh_3)_2](BPh_4)_2$ type (L = phosphites) were prepared using the mixed-ligand hydrides $ReH_2(NO)L(PPh_3)_2$ as precursors. Mononuclear $[ReH(ArN{=}NH)(NO)L(PPh_3)_2]BPh_4$ monodiazene and binuclear $[\{ReH(NO)L(PPh_3)_2\}_2(\mu\text{-}HN{=}NAr{-}ArN{=}NH)](BPh_4)_2$ species, with aryldiazene as a bridging ligand, were also prepared by an analogous procedure.

The hydride-aryldiazenido $[ReH(C_6H_5N_2)\{PPh(OEt)_2\}_4]BPh_4$ complex was also obtained from the reaction of trihydride ReH_3P_4 with a aryldiazonium cation.

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