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FULL PAPER

Synthesis and reactivity of hydrazine complexes of iridium(III)

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Hydride complexes $IrHCl_2[PPh(OEt)_2]L_2$ **1**, **3** and $IrHCl_2[P(OEt)_3]L_2$ **2**, **4** (L = PPh_3 or $AsPh_3$) were prepared by substituting one phosphine or arsine ligand in $IrHCl_2L_3$ with the appropriate phosphite. Treatment of hydrides **1**–**4** first with triflic acid (CF_3SO_3H) and then with hydrazines gave $[IrCl_2(RNHNH_2)\{PPh(OEt)_2\}L_2]BPh_4$ **5**, **7** and $[IrCl_2(RNHNH_2)\{P(OEt)_3\}L_2]BPh_4$ **6**, **8** (R = H, Me, Ph or $C_6H_4NO_2$-4). Hydride–hydrazine complexes $[IrH_2(RNHNH_2)(PPh_3)_3]BPh_4$ **9** and $[IrHCl(RNHNH_2)(PPh_3)_2]BPh_4$ **10** (R = H, Me or Ph) were also prepared by allowing $IrH_3(PPh_3)_3$ or $IrH_2Cl(PPh_3)_3$ to react sequentially first with CF_3SO_3H or $HBF_4{\cdot}Et_2O$ and then with the appropriate hydrazine. All complexes were fully characterised by IR and NMR spectroscopy and their geometry in solution was also established. Oxidation with $Pb(OAc)_4$ at −30 °C of arylhydrazines $[IrCl_2(ArNHNH_2)L'L_2]BPh_4$ **5**–**8** [L′ = $PPh(OEt)_2$ or $P(OEt)_3$; Ar = Ph] afforded stable aryldiazene derivatives $[IrCl_2(ArN{=}NH)\{PPh(OEt)_2\}L_2]BPh_4$ **11**, **13** and $[IrCl_2(ArN{=}NH)\{P(OEt)_3\}L_2]BPh_4$ **12**, **14**. By contrast, treatment with $Pb(OAc)_4$ at −30 °C of methylhydrazine complexes $[IrCl_2(MeNHNH_2)L'L_2]BPh_4$ gave hydrides $IrHCl_2L'L_2$. Aryldiazene complexes $[IrCl_2(ArN{=}NH)L'L_2]BPh_4$ **11**–**14** and $[\{IrCl_2L'L_2\}_2(\mu\text{-}HN{=}NAr\text{–}ArN{=}NH)](BPh_4)_2$ **15**–**18** [Ar = Ph or C_6H_4Me-4; Ar–Ar = 4,4′-C_6H_4–C_6H_4 or 4,4′-(2-Me)C_6H_3–C_6H_3(Me-2)] were also prepared by allowing hydride species $IrHCl_2L'L_2$ **1**–**4** to react with the appropriate aryldiazonium cations in acetone at −80 °C. Their characterisation by IR and NMR spectroscopy (with ^{15}N isotopic substitution) is discussed.

Transition metal complexes containing hydrazine and other partially reduced dinitrogen ligands such as diazene RN=NH and diazenido RN_2 constitute a research area of current interest, due not only to the relationship with intermediates of the dinitrogen fixation process, but also to the diverse reactivity modes and structural properties that these "diazo" complexes exhibit.[1,2] Numerous studies have been reported in the past 25 years on the synthesis, structure and reactivity of this class of complexes, but relatively few of them have involved hydrazine derivatives.[1–3] Coordinated hydrazine NH_2NH_2 has been proposed as possible intermediate in nitrogen fixation, has been shown to be a substrate[4] as well as a product of functioning nitrogenase, and has been isolated by quenching the enzyme.[5] However, much remains to be known about the chemistry of coordinated hydrazine and it is therefore of interest to report new results in this field, including the synthesis and reactivity of the first hydrazine complexes of iridium. A glance through the literature shows that the "diazo" chemistry of iridium involves mainly aryldiazene, aryldiazenido and diazoalkane complexes,[6] the coordination chemistry of hydrazine being practically unexplored for this metal.

In previous papers[7] we reported the synthesis, structure and reactivity of "diazo" complexes of several transition metals, including hydrazine derivatives of the iron family[8] of the type $[MH(RNHNH_2)L'_4]^+$, $[M(RNHNH_2)_2L'_4]^{2+}$ and $[M(RCN)(RNHNH_2)L'_4]^{2+}$ (L′ = phosphite). We have now extended these studies to other d^6 transition metals, with the aim of first establishing a method for synthesis, and then investigating the properties of the hydrazine complexes of these metals. Results on iridium, involving the synthesis of both hydrazine and aryldiazene derivatives, are reported here.

Experimental

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 stable in air and were stored at room temperature. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. The $IrCl_3{\cdot}3H_2O$ was a Pressure Chemical Co. product, used as received. Triethylphosphite $P(OEt)_3$ (Aldrich) was purified by distillation under nitrogen; $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon.[9] Hydrazines $PhNHNH_2$, $MeNHNH_2$, 4-$NO_2C_6H_4NHNH_2$ and Me_2NNH_2 were Aldrich products used as received. Hydrazine NH_2NH_2 was prepared by decomposition of hydrazine cyanurate $NH_2NH_2{\cdot}C_3H_3N_3O_3$ (Fluka) following the reported method.[10] Diazonium salts $[ArN_2]^+BF_4^-$ were obtained in the usual way.[11] The related bis(diazonium) $[N_2Ar\text{–}ArN_2](BF_4)_2$ [Ar–Ar = 4,4′-C_6H_4–C_6H_4 or 4,4′-(2-Me)C_6H_3–C_6H_3(Me-2)] salts were prepared by treating the amine precursors $H_2NAr\text{–}ArNH_2$ with $NaNO_2$, as described in the literature for common monodiazonium salts.[11] Labelled diazonium tetrafluoroborates $[PhN{\equiv}^{15}N]BF_4$ and $[4,4'\text{-}^{15}N{\equiv}NC_6H_4\text{–}C_6H_4N{\equiv}^{15}N](BF_4)_2$ were prepared from $Na^{15}NO_2$ (99% enriched, CIL) and the appropriate amine. Alternatively, the $[Ph^{15}N{\equiv}N]BF_4$ salt was obtained from $NaNO_2$ and $Ph^{15}NH_2$. Triflic acid (Aldrich) and $HBF_4{\cdot}Et_2O$ (54% solution in Et_2O, Fluka) were used as received. Other reagents were purchased from commercial sources in the highest available purity and used as received. IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer. NMR spectra (^1H, ^{31}P) 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. $^{31}P\text{-}\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The SwaN-MR software package[12] was used to treat NMR data. The conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in $MeNO_2$ at 25 °C were measured with a Radiometer CDM 83 instrument.

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Synthesis of complexes

Hydrides *mer*-$IrHCl_2(PPh_3)_3$, *mer*-$IrHCl_2(AsPh_3)_3$, $IrH_2Cl(PPh_3)_3$ and $IrH_3(PPh_3)_3$ were prepared following the methods previously reported.[13a–c]

$IrHCl_2[PPh(OEt)_2](PPh_3)_2$ 1 and $IrHCl_2[P(OEt)_3](PPh_3)_2$ 2. An excess of the appropriate phosphite (4.75 mmol) was added to a solution of $IrHCl_2(PPh_3)_3$ (1 g, 0.95 mmol) in 30 cm^3 of benzene and the reaction mixture refluxed for 2 h. The solution was removed under reduced pressure, giving an oil which was triturated with 3 cm^3 of ethanol. A yellow solid slowly separated out from the resulting solution, which was filtered off and crystallised from benzene (3 cm^3)–ethanol (5 cm^3); yield ≥60% (Found: C, 55.8; H, 4.6; Cl, 7.35. $C_{46}H_{46}Cl_2IrO_2P_3$ **1** requires C, 56.0; H, 4.70; Cl, 7.2. Found: C, 52.95; H, 4.8; Cl, 7.20. $C_{42}H_{46}Cl_2IrO_3P_3$ **2** requires C, 52.8; H, 4.9; Cl, 7.4%).

$IrHCl_2[PPh(OEt)_2](AsPh_3)_2$ 3 and $IrHCl_2[P(OEt)_3](AsPh_3)_2$ 4. An excess of the appropriate phosphite (4.22 mmol) was added to a solution of $IrHCl_2(AsPh_3)_3$ (1 g, 0.845 mmol) in 20 cm^3 of benzene and the reaction mixture refluxed for 2 h. The solvent was removed under reduced pressure, giving a yellow solid which was treated with ethanol (15 cm^3) containing an excess of $NaBH_4$ (0.15 g, 4.0 mmol). The resulting mixture was refluxed for 1 h and the solvent was then removed under reduced pressure. The residual solid material was treated with ethanol (4 cm^3) to give a yellow solution which was vigorously stirred until a solid separated out. This was filtered off and crystallised from benzene (2 cm^3)–ethanol (4 cm^3); yield ≥45% (Found: C, 51.25; H, 4.3; Cl, 6.4. $C_{46}H_{46}As_2Cl_2IrO_2P$ **3** requires C, 51.40; H, 4.3; Cl, 6.60. Found: C, 48.6; H, 4.5; Cl, 6.7. $C_{42}H_{46}As_2Cl_2IrO_3P$ **4** requires C, 48.4; H, 4.45; Cl, 6.80%).

$[IrCl_2(RNHNH_2)\{PPh(OEt)_2\}(PPh_3)_2]BPh_4$ 5 and $[IrCl_2(RNHNH_2)\{P(OEt)_3\}(PPh_3)_2]BPh_4$ 6 (R = H a, Me b, Ph c or $C_6H_4NO_2$-4 d). To a solution of the appropriate hydride (0.50 mmol) in 20 cm^3 of CH_2Cl_2, cooled to −80 °C, was added an equimolar amount of CF_3SO_3H (44 μL, 0.50 mmol) and the reaction mixture, brought to room temperature, was stirred for *ca.* 1 h. An excess of the appropriate hydrazine $RNHNH_2$ (1.0 mmol for NH_2NH_2, 5 mmol for 4-$NO_2C_6H_4NHNH_2$) was added and, after 2–3 h of stirring, the solvent was removed under reduced pressure. The resulting oil was triturated with ethanol (5 cm^3) containing an excess of $NaBPh_4$ (0.34 g, 1 mmol). A white solid slowly separated out, which was filtered off and crystallised from CH_2Cl_2 (3 cm^3)–ethanol (5 cm^3); yield 60–70%: Λ_M/S cm^2 mol^{-1} = 54.7 for **5a**, 54.5 for **5b**, 51.9 for **5c**, 53.5 for **5d**, 50.9 for **6b**, 53.7 for **6c**, 54.0 for **6d** (Found: C, 62.7; H, 5.25; N, 2.0; Cl, 5.1. $C_{70}H_{69}BCl_2IrN_2O_2P_3$ **5a** requires C, 62.9; H, 5.20; N, 2.1; Cl, 5.30. Found: C, 63.0; H, 5.05; N, 2.0; Cl, 5.0. $C_{71}H_{71}BCl_2IrN_2O_2P_3$ **5b** requires C, 63.1; H, 5.30; N, 2.1; Cl, 5.25. Found: C, 64.8; H, 5.1; N, 1.9; Cl, 5.2. $C_{76}H_{73}BCl_2IrN_2O_2P_3$ **5c** requires C, 64.6; H, 5.20; N, 2.0; Cl, 5.0. Found: C, 62.4; H, 4.90; N, 3.05; Cl, 5.1. $C_{76}H_{72}BCl_2IrN_3O_4P_3$ **5d** requires C, 62.60; H, 5.0; N, 2.9; Cl, 4.9. Found: C, 61.2; H, 5.30; N, 2.0; Cl, 5.3. $C_{67}H_{71}BCl_2IrN_2O_3P_3$ **6b** requires C, 61.00; H, 5.4; N, 2.1; Cl, 5.4. Found: C, 62.45; H, 5.4; N, 1.9; Cl, 5.2. $C_{72}H_{73}BCl_2IrN_2O_3P_3$ **6c** requires C, 62.6; H, 5.3; N, 2.0; Cl, 5.1. Found: C, 60.8; H, 5.1; N, 3.0; Cl, 4.9. $C_{72}H_{72}BCl_2IrN_3O_5P_3$ **6d** requires C, 60.6; H, 5.1; N, 2.95; Cl, 5.0%).

$[IrCl_2(NH_2NH_2)\{P(OEt)_3\}(PPh_3)_2]BPh_4$ 6a. This complex was obtained by slight modification of the general method. To a solution of $IrHCl_2[P(OEt)_3](PPh_3)_2$ (0.191 g, 0.20 mmol) in 10 cm^3 of toluene, cooled to −80 °C, was added an equimolar amount of CF_3SO_3H (18 μL, 0.20 mmol) and the reaction mixture was brought to room temperature. Dichloromethane (5 cm^3) was added and, after 1 h of stirring, an excess of NH_2NH_2 (13 μL, 0.40 mmol) was also added. The reaction mixture was stirred for 2 h and the solvent was then removed under reduced pressure, leaving an oily product which was treated with ethanol (2 cm^3). The addition of an excess of $NaBPh_4$ (0.137 g, 0.40 mmol) caused the separation of a white solid which was filtered off and crystallised from CH_2Cl_2 (2 cm^3)–ethanol (5 cm^3); yield ≥65%; Λ_M = 52.4 S cm^2 mol^{-1} (Found: C, 60.9; H, 5.35; N, 2.1; Cl, 5.2. $C_{66}H_{69}BCl_2IrN_2O_3P_3$ requires C, 60.7; H, 5.3; N, 2.15; Cl, 5.4%).

$[IrCl_2(Me_2NNH_2)\{P(OEt)_3\}(PPh_3)_2]BPh_4$ 6e. This complex was prepared similarly to related compounds **6**, but using a large excess of Me_2NNH_2 (10:1 ratio) and a longer reaction time (7–8 h); yield ≥30%; Λ_M = 59.2 S cm^2 mol^{-1} (Found: C, 61.0; H, 5.6; N, 2.2; Cl, 5.5. $C_{68}H_{73}BCl_2IrN_2O_3P_3$ requires C, 61.3; H, 5.5; N, 2.10; Cl, 5.3%).

$[IrCl_2(RNHNH_2)\{PPh(OEt)_2\}(AsPh_3)_2]BPh_4$ 7 and $[IrCl_2(RNHNH_2)\{P(OEt)_3\}(AsPh_3)_2]BPh_4$ 8 (R = H a, Me b or Ph c). These complexes were prepared in the same manner as the related triphenylphosphine complexes, with yields varying between 40 and 60%; Λ_M/S cm^2 mol^{-1} = 49.8 for **7a**, 48.4 for **7c**, 51.4 for **8a**, 48.6 for **8b**, 46.3 for **8c** (Found: C, 59.2; H, 4.85; N, 1.9; Cl, 5.15. $C_{70}H_{69}As_2BCl_2IrN_2O_2P$ **7a** requires C, 59.00; H, 4.9; N, 2.0; Cl, 5.0. Found: C, 60.7; H, 5.0; N, 2.0; Cl, 4.6. $C_{70}H_{73}As_2BCl_2IrN_2O_2P$ **7c** requires C, 60.8; H, 4.90; N, 1.9; Cl, 4.7. Found: C, 56.75; H, 4.95; N, 2.1; Cl, 5.2. $C_{70}H_{69}As_2BCl_2IrN_2O_2P$ **8a** requires C, 56.9; H, 5.0; N, 2.0; Cl, 5.1. Found: C, 57.4; H, 4.9; N, 2.1; Cl, 4.9. $C_{67}H_{71}As_2BCl_2IrN_2O_3P$ **8b** requires C, 57.2; H, 5.1; N, 2.0; Cl, 5.0. Found: C, 59.1; H, 5.2; N, 2.0; Cl, 4.9. $C_{72}H_{73}As_2BCl_2IrN_2O_3P$ **8c** requires C, 58.9; H, 5.0; N, 1.9; Cl, 4.8%).

$[IrH_2(RNHNH_2)(PPh_3)_3]BPh_4$ 9 (R = H a or Me b). To a solution of $IrH_3(PPh_3)_3$ (0.150 g, 0.153 mmol) in 5 cm^3 of toluene, cooled to −80 °C, was added an equimolar amount of CF_3SO_3H (13 μL, 0.153 mmol) and the reaction mixture brought to room temperature. After the addition of 5 cm^3 of CH_2Cl_2, the reaction mixture was stirred for 1 h and then an excess of the appropriate hydrazine (0.4 mmol) added. After 4 h of stirring, the solvent was removed under reduced pressure, and the resulting oil treated with 5 cm^3 of ethanol. The addition of an excess of $NaBPh_4$ (0.103 g, 0.3 mmol) in 3 cm^3 of ethanol to the solution caused the precipitation of a white solid, which was filtered off and crystallised from CH_2Cl_2 (3 cm^3)–ethanol (7 cm^3); yield ≥55%; Λ_M/S cm^2 mol^{-1} = 51.7 for **9a**, 57.3 for **9b** (Found: C, 70.1; H, 5.3; N, 2.15. $C_{78}H_{71}BIrN_2P_3$ **9a** requires C, 70.3; H, 5.4; N, 2.10. Found: C, 70.60; H, 5.4; N, 2.25. $C_{79}H_{73}BIrN_2P_3$ **9b** requires C, 70.5; H, 5.5; N, 2.1%).

$[IrHCl(RNHNH_2)(PPh_3)_2]BPh_4$ 10 (R = H a, Me b or Ph c). To a solution of $IrH_2Cl(PPh_3)_3$ (0.102 g, 0.1 mmol) in 10 cm^3 of CH_2Cl_2, cooled to −80 °C, was added an equimolar amount of $HBF_4\cdot Et_2O$ (13.5 μL, 0.1 mmol) and the reaction mixture, brought to room temperature, was stirred for *ca.* 90 min. An excess of the appropriate hydrazine (0.3 mmol) was added and, after 3 h of stirring, the solvent was removed under reduced pressure. The resulting solid was treated with 5 cm^3 of ethanol containing an excess of $NaBPh_4$ (0.068 g, 0.2 mmol). The solution was vigorously stirred until a white solid separated out, which was filtered off and crystallised from CH_2Cl_2 (2 cm^3)–ethanol (6 cm^3); yield ≥60%; Λ_M/S cm^2 mol^{-1} = 53.9 for **10a**, 50.4 for **10b**, 52.5 for **10c** (Found: C, 65.0; H, 5.2; N, 2.4; Cl, 3.2. $C_{60}H_{55}BClIrN_2P_2$ **10a** requires C, 65.25; H, 5.0; N, 2.5; Cl, 3.2. Found: C, 65.3; H, 5.0; N, 2.65; Cl, 3.3. $C_{61}H_{57}BClIrN_2P_2$ **10b** requires C, 65.50; H, 5.1; N, 2.50; Cl, 3.2. Found: C, 66.9; H, 5.05; N, 2.3; Cl, 3.1. $C_{66}H_{59}BClIrN_2P_2$ **10c** requires C, 67.1; H, 5.0; N, 2.4; Cl, 3.00%).

[IrCl$_2$(ArN=NH){PPh(OEt)$_2$}L$_2$]BPh$_4$ 11, 13 and [IrCl$_2$(ArN=NH){P(OEt)$_3$}L$_2$]BPh$_4$ 12, 14 (Ar = Ph c or C$_6$H$_4$Me-4 f; L = PPh$_3$ 11, 12 or AsPh$_3$ 13, 14). In a 25 cm^3 three-necked round-bottomed flask were placed the appropriate hydride IrHCl$_2${PPh(OEt)$_2$}L$_2$ or IrHCl$_2${P(OEt)$_3$}L$_2$ (L = PPh$_3$ or AsPh$_3$) (0.1 mmol) and the aryldiazonium salt ArN$_2$$^+BF_4$$^-$ in an equimolar amount (0.1 mmol). The flask was cooled to −80 °C and dichloromethane (10 cm^3) was slowly added. The reaction mixture was brought to 0 °C, stirred at this temperature for 3 h, and the solvent was then removed under reduced pressure. The resulting oil was dissolved in 3 cm^3 of ethanol and an excess of NaBPh$_4$ (0.068 g, 0.2 mmol) in 2 cm^3 of ethanol added. A yellow or orange solid slowly separated out from the stirred solution, which was filtered off and crystallised from CH$_2$Cl$_2$ (3 cm^3)–ethanol (7 cm^3); yields varied between 55 and 70%; Λ_M/S cm^2 mol^{-1} = 56.4 for **11c**, 57.9 for **11f**, 55.4 for **12c**, 58.6 for **12f**, 55.4 for **13c**, 54.3 for **14c**, 51.9 for **14f** (Found: C, 64.6; H, 5.15; N, 1.9; Cl, 5.2. C$_{76}$H$_{71}$BCl$_2$IrN$_2$O$_2$P$_3$ **11c** requires C, 64.7; H, 5.1; N, 2.0; Cl, 5.0. Found: C, 64.85; H, 5.2; N, 2.05; Cl, 5.1. C$_{77}$H$_{73}$BCl$_2$IrN$_2$O$_2$P$_3$ **11f** requires C, 64.9; H, 5.2; N, 2.0; Cl, 5.0. Found: C, 62.9; H, 5.1; N, 2.1; Cl, 5.25. C$_{72}$H$_{71}$BCl$_2$IrN$_2$O$_3$P$_3$ **12c** requires C, 62.70; H, 5.2; N, 2.0; Cl, 5.1. Found: C, 62.8; H, 5.4; N, 1.9; Cl, 5.2. C$_{73}$H$_{73}$BCl$_2$IrN$_2$O$_3$P$_3$ **12f** requires C, 62.9; H, 5.3; N, 2.0; Cl, 5.1. Found: C, 61.5; H, 4.70; N, 1.85; Cl, 4.8. C$_{76}$H$_{71}$As$_2$BCl$_2$IrN$_2$O$_2$P **13c** requires C, 60.9; H, 4.8; N, 1.9; Cl, 4.7. Found: C, 60.1; H, 5.0; N, 1.8; Cl, 4.9. C$_{72}$H$_{71}$As$_2$BCl$_2$IrN$_2$O$_3$P **14c** requires C, 58.9; H, 4.9; N, 1.9; Cl, 4.8. Found: C, 59.4; H, 4.9; N, 2.00; Cl, 4.65. C$_{73}$H$_{73}$As$_2$BCl$_2$IrN$_2$O$_3$P **14f** requires C, 59.20; H, 5.0; N, 1.9; Cl, 4.8%).

[IrCl$_2$(PhN=^{15}NH){PPh(OEt)$_2$}(PPh$_3$)$_2$]BPh$_4$ 11c$_1$ and [IrCl$_2$(Ph^{15}N=NH){PPh(OEt)$_2$}(PPh$_3$)$_2$]BPh$_4$ 11c$_2$. These complexes were obtained in the same manner as the related unlabelled complex **11c** using the PhN≡^{15}N$^+$BF$_4$$^-$ or Ph^{15}N≡N$^+$BF$_4$$^-$ phenyldiazonium salts; yield ≥70%.

[{IrCl$_2$[PPh(OEt)$_2$]L$_2$}$_2$(μ-4,4′-HN=NC$_6$H$_4$–C$_6$H$_4$N=NH)](BPh$_4$)$_2$ 15c, 17c and [{IrCl$_2$[P(OEt)$_3$]L$_2$}$_2$(μ-4,4′-HN=NC$_6$H$_4$–C$_6$H$_4$N=NH)](BPh$_4$)$_2$ 16c, 18c (L = PPh$_3$ 15, 16 or AsPh$_3$ 17, 18). These complexes were prepared following the method used for related mononuclear compounds **11**–**14** by reacting hydrides IrHCl$_2$[PPh(OEt)$_2$]L$_2$ and IrHCl$_2$[P(OEt)$_3$]L$_2$ (0.1 mmol) with the bis(aryldiazonium) [N$_2$Ar–ArN$_2$](BF$_4$)$_2$ salt (0.05 mmol) in CH$_2$Cl$_2$; yield ≥40%; Λ_M/S^2 cm^2 mol^{-1} = 119.7 for **15c**, 128.7 for **16c**, 125.4 for **17c**, 125.4 for **18c** (Found: C, 64.8; H, 5.1; N, 2.05; Cl, 4.8. C$_{152}$H$_{140}$B$_2$Cl$_4$Ir$_2$N$_4$O$_4$P$_6$ **15c** requires C, 64.7; H, 5.00; N, 2.0; Cl, 5.0. Found: C, 62.9; H, 4.95; N, 1.9; Cl, 5.0. C$_{144}$H$_{140}$B$_2$Cl$_4$Ir$_2$N$_4$O$_6$P$_6$ **16c** requires C, 62.75; H, 5.1; N, 2.0; Cl, 5.1. Found: C, 60.8; H, 4.60; N, 1.9; Cl, 5.0. C$_{152}$H$_{140}$As$_4$B$_2$Cl$_4$Ir$_2$N$_4$O$_4$P$_2$ **17c** requires C, 60.9; H, 4.7; N, 1.9; Cl, 4.7. Found: C, 59.2; H, 4.9; N, 1.8; Cl, 4.7. C$_{144}$H$_{140}$As$_4$B$_2$Cl$_4$Ir$_2$N$_4$O$_6$P$_2$ **18c** requires C, 59.0; H, 4.8; N, 1.9; Cl, 4.8%).

[{IrCl$_2$[PPh(OEt)$_2$](PPh$_3$)$_2$}$_2$(μ-4,4′-H^{15}N=NC$_6$H$_4$–C$_6$H$_4$N=^{15}NH)](BPh$_4$)$_2$ 15c$_1$. This complex was prepared in the same manner as for the related unlabelled compound **15c** using the [4,4′-^{15}N≡NC$_6$H$_4$–C$_6$H$_4$N≡^{15}N](BF$_4$)$_2$ bis(diazonium) salt.

[{IrCl$_2$[PPh(OEt)$_2$](PPh$_3$)$_2$}$_2$(μ-4,4′-HN=N(2-Me)C$_6$H$_3$–C$_6$H$_3$(Me-2)N=NH}](BF$_4$)$_2$ 15f. A 25 cm^3 three-necked round bottomed flask was charged with 0.100 g (0.10 mmol) of IrHCl$_2$[PPh(OEt)$_2$](PPh$_3$)$_2$ and 0.020 g (0.05 mmol) of [4,4′-N$_2$(2-Me)C$_6$H$_3$–C$_6$H$_3$(Me-2)N$_2$](BF$_4$)$_2$ and cooled to −80 °C. Acetone (15 cm^3) was added and the reaction mixture, slowly brought to room temperature, was stirred for 8 h. The solution was filtered and the solvent removed under reduced pressure. The resulting reddish-brown oil was triturated with ethanol (3 cm^3) until a red solid separated out, which was filtered off and crystallised from CH$_2$Cl$_2$ (2 cm^3)–ethanol (5 cm^3); yield ≥40%; Λ_M = 184.7 S cm^2 mol^{-1} (Found: C, 53.2; H, 4.3; N, 2.25; Cl, 6.1. C$_{106}$H$_{104}$B$_2$Cl$_4$F$_8$Ir$_2$N$_4$O$_4$P$_6$ requires C, 53.4; H, 4.40; N, 2.35; Cl, 5.95%).

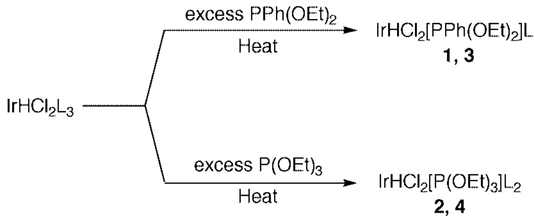
Oxidation of hydrazine complexes

Reactions were carried out in CH$_2$Cl$_2$ at −30 °C using Pb(OAc)$_4$ as oxidising agent. In a typical reaction, solid samples of the appropriate hydrazine complexes **5**–**10** (0.1 mmol) were placed singly in a three-necked 25 cm^3 round-bottomed flask fitted with a solid-addition sidearm containing an excess of Pb(OAc)$_4$ (0.14 g, 0.30 mmol). Dichloromethane (10 cm^3) was added, the solution cooled to −30 °C, and the Pb(OAc)$_4$ added in portions over 20–30 min to the cold stirred solution. The reaction mixture was then brought to room temperature and filtered, and the solvent was removed under reduced pressure, giving an oil. The addition of ethanol (3 cm^3) containing an excess of NaBPh$_4$ (0.068 g, 0.2 mmol) led to the separation of a solid, which was filtered off and crystallised from CH$_2$Cl$_2$ (2–3 cm^3)–ethanol (4–6 cm^3).

Results and discussion

Preparation of hydride complexes

The synthesis of hydrazine complexes of iridium was achieved using as precursors the new hydrides IrHCl$_2$[PPh(OEt)$_2$]L$_2$ **1**, **3** and IrHCl$_2$[P(OEt)$_3$]L$_2$ **2**, **4** (L = PPh$_3$ or AsPh$_3$), the preparation of which deserves some comment. Treatment of the monohydride[13a,c] IrHCl$_2$L$_3$ with an excess of phosphite gives the mixed-ligand species **1**–**4** as shown in Scheme 1.



Scheme 1 L = PPh$_3$ **1**, **2** or AsPh$_3$ **3**, **4**.

The reaction proceeds with the replacement of only one PPh$_3$ or AsPh$_3$ ligand, and the formation exclusively of monophosphite species **1**–**4** which may be isolated as yellow solids and characterised. The complexes are air-stable diamagnetic solids, very soluble in aromatic hydrocarbons and slightly in CH$_2$Cl$_2$ or THF, and non-electrolytes. The analytical and spectroscopic data (Table 1) support the proposed formulations. In the low frequency region, the ^{1}H NMR spectra of PPh$_3$ derivatives **1**, **2** show one doublet of triplets at δ −10.49 for **1** and δ −10.38 for **2**, attributed to the hydride ligand coupled with the phosphorus nuclei. By contrast, in related AsPh$_3$ compounds **3**, **4**, the ^{1}H NMR hydride signal appears as only one sharp doublet at δ −9.80 and −9.67, respectively, due to coupling with only one phosphite ligand. For compounds **1** and **2**, the ^{31}P-{^{1}H} NMR spectra show an AB$_2$ pattern, formed of a doublet at δ *ca.* −2 attributed to the PPh$_3$, and a triplet at δ 102.0 or 79.9 due to the PPh(OEt)$_2$ or P(OEt)$_3$ ligand. Only one singlet at δ 82.0 or 85.6 ppm is observed, instead, in the spectra of AsPh$_3$ derivatives **3**, **4**. These spectroscopic data fit the proposed formulations, but do not allow any geometry to be unambiguously proposed. However, we identified[14] ν(IrCl) bands in the far-IR spectra of **1**, appearing as two absorptions of weak intensity at 333 and 326 cm^{-1} (Table 1), in accord with the presence of two Cl$^-$ ligands in a mutually *cis* position. Taking into account the fact that the proton NMR spectra of **1**–**4** show high values (220–265 Hz) for one of the J_{PH} coupling constants, indicating a mutually *trans* position of the hydride and of one phosphine ligand, a *fac* geometry (Fig. 1) may be proposed for the hydride derivatives.

Table 1 IR and NMR spectroscopic data for the iridium complexes

		IR^{a}		^{1}H NMR^{b,c}			^{31}P-{^{1}H} NMR^{b,d}
	Compound	ν/cm^{-1}	Assignment	δ(J/Hz)	Assignment	Spin system	δ(J/Hz)
1	IrHCl$_2$[PPh(OEt)$_2$](PPh$_3$)$_2$	2116w	ν(IrH)	3.84 (m), 3.51 (m)	CH$_2$	AB$_2$^{e}	δ_A 102.0
		(333w)	ν(IrCl)	0.98 (t)	CH$_3$		δ_B −2.4
		(326w)		−10.49 (dt,	IrH		J_{AB} = 16
				$J_{PH_{trans}}$ = 220,			
				$J_{PH_{cis}}$ = 15)^{e}			
2	IrHCl$_2$[P(OEt)$_3$](PPh$_3$)$_2$	2073w	ν(IrH)	3.58 (qnt)	CH$_2$	AB$_2$^{e}	δ_A 79.9
				0.92 (t)	CH$_3$		δ_B −1.66
				−10.38 (dt,	IrH		J_{AB} = 22
				$J_{PH_{trans}}$ = 262,			
				$J_{PH_{cis}}$ = 16)^{e}			
3	IrHCl$_2$[PPh(OEt)$_2$](AsPh$_3$)$_2$	2065w	ν(IrH)	3.92 (m)	CH$_2$	A^{e}	82.0 (s)
				3.49 (m)			
				0.99 (t)	CH$_3$		
				−9.80 (d,	IrH		
				J_{PH} = 225)^{e}			
4	IrHCl$_2$[P(OEt)$_3$](AsPh$_3$)$_2$	2051w	ν(IrH)	3.70 (qnt)	CH$_2$	A^{e}	85.6 (s)
				0.92 (t)	CH$_3$		
				−9.67 (d,	IrH		
				J_{PH} = 265)^{e}			
5a	[IrCl$_2$(NH$_2$NH$_2$){PPh(OEt)$_2$}(PPh$_3$)$_2$]BPh$_4$	3342w	ν(NH)	4.22 (br)	IrNH$_2$	AB$_2$	δ_A 63.4
		3276m		3.45 (m)	CH$_2$		δ_B −22.6
		3263w		3.07 (m, br)	NH$_2$		J_{AB} = 22
		3226w		1.18 (t)	CH$_3$		
		(338m)	ν(IrCl)				
5b	[IrCl$_2$(MeNHNH$_2$){PPh(OEt)$_2$}(PPh$_3$)$_2$]BPh$_4$	3329w	ν(NH)	3.98 (br)	IrNH$_2$	AB$_2$	δ_A 62.2
		3248m		3.80 (m)	NH		δ_B −22.2
		3240w		3.38 (m)	CH$_2$		J_{AB} = 21
				1.56 (d, J_{HH} = 8)	CH$_3$ hydraz		
				1.07 (t)	CH$_3$ phos		
5c	[IrCl$_2$(PhNHNH$_2$){PPh(OEt)$_2$}(PPh$_3$)$_2$]BPh$_4$	3302w	ν(NH)	6.49 (br)	NH	AB$_2$	δ_A 61.1
		3241m		4.57 (br)	IrNH$_2$		δ_B −22.7
		3197w		3.47 (m)	CH$_2$		J_{AB} = 22
		1604m	δ(NH$_2$)	1.13 (t)	CH$_3$		
5d	[IrCl$_2$(4-NO$_2$C$_6$H$_4$NHNH$_2$){PPh(OEt)$_2$}-(PPh$_3$)$_2$]BPh$_4$	3311m	ν(NH)	4.49 (br)	IrNH$_2$	AB$_2$	δ_A 59.9
		3230m		3.45 (m)	CH$_2$		δ_B −23.2
		1602m	δ(NH$_2$)	1.09 (t)	CH$_3$		J_{AB} = 22
6a	[IrCl$_2$(NH$_2$NH$_2$){P(OEt)$_3$}(PPh$_3$)$_2$]BPh$_4$	3342m	ν(NH)	4.12 (m)	IrNH$_2$	AB$_2$	δ_A 30.8
		3270m		3.43 (qnt)	CH$_2$		δ_B −18.7
		3250(sh)		3.08 (br)	NH$_2$		J_{AB} = 26
		(327w)	ν(IrCl)	0.99 (t)	CH$_3$		
6b	[IrCl$_2$(MeNHNH$_2$){P(OEt)$_3$}(PPh$_3$)$_2$]BPh$_4$	3302m	ν(NH)	3.94 (m)	IrNH$_2$	AB$_2$	δ_A 28.7
		3256m		3.80 (m)	NH		δ_B −18.0
		3197m		3.42 (qnt)	CH$_2$		J_{AB} = 26
				1.61 (d, J_{HH} = 4)	CH$_3$ hydraz		
				0.99 (t)	CH$_3$ phos		
6c	[IrCl$_2$(PhNHNH$_2$){P(OEt)$_3$}(PPh$_3$)$_2$]BPh$_4$	3317m	ν(NH)	6.40 (m)	NH	AB$_2$	δ_A 28.1
		3257m		4.45 (m)	IrNH$_2$		δ_B −18.9
		3197w		3.44 (qnt)	CH$_2$		J_{AB} = 26
		1601m	δ(NH$_2$)	1.00 (t)	CH$_3$		
6d	[IrCl$_2$(4-NO$_2$C$_6$H$_4$NHNH$_2$){P(OEt)$_3$}-(PPh$_3$)$_2$]BPh$_4$	3282m	ν(NH)	4.40 (m)	IrNH$_2$	AB$_2$	δ_A 26.0
		3227w		3.47 (qnt)	CH$_2$		δ_B −19.5
		1602m	δ(NH$_2$)	1.01 (t)	CH$_3$		J_{AB} = 26
6e	[IrCl$_2$(Me$_2$NNH$_2$){P(OEt)$_3$}(PPh$_3$)$_2$]BPh$_4$	3310w	ν(NH)	4.12 (br)	IrNH$_2$	AB$_2$	δ_A 21.5
		3233m		3.55 (qnt)	CH$_2$		δ_B −17.4
		1616m	δ(NH$_2$)	2.39 (s)	CH$_3$ hydraz		J_{AB} = 20
				1.06 (t)	CH$_3$ phos		
7a	[IrCl$_2$(NH$_2$NH$_2$){PPh(OEt)$_2$}(AsPh$_3$)$_2$]BPh$_4$	3340m	ν(NH)	4.45 (m)	IrNH$_2$	A	63.6 (s)
		3271m		3.48 (qnt)	CH$_2$		
		3263w		3.29 (m)	NH$_2$		
		3223m		1.01 (t)	CH$_3$		
7c	[IrCl$_2$(PhNHNH$_2$){PPh(OEt)$_2$}(AsPh$_3$)$_2$]BPh$_4$	3299m	ν(NH)	6.64 (m)	NH	A	61.4 (s)
		3242m		4.75 (t, br)	IrNH$_2$		
		3197w		3.54 (qnt)	CH$_2$		
		1597m	δ(NH$_2$)	1.10 (t)	CH$_3$		
		(332w)	ν(IrCl)				
8a	[IrCl$_2$(NH$_2$NH$_2$){P(OEt)$_3$}(AsPh$_3$)$_2$]BPh$_4$	3347w	ν(NH)	4.39 (m)	IrNH$_2$	A	31.6 (2)
		3263m		3.57 (m)	CH$_2$		
		3230m		3.36 (m)	NH$_2$		
		3158w		1.00 (t)	CH$_3$		
8b	[IrCl$_2$(MeNHNH$_2$){P(OEt)$_3$}(AsPh$_3$)$_2$]BPh$_4$	3308w	ν(NH)	4.10 (m)	NH	A	30.1 (s)
		3244m		4.21 (m)	IrNH$_2$		
		3202w		3.58 (qnt)	CH$_2$		
		1597m	δ(NH$_2$)	1.73 (d,	CH$_3$ hydraz		
		(335w)	ν(IrCl)	J_{HH} = 6)			
				1.00 (t)	CH$_3$ phos		

Table 1 (*Contd.*)

		IR[a]		^{1}H NMR[b,c]			^{31}P-{^{1}H} NMR[b,d]
	Compound	ν/cm^{-1}	Assignment	δ(J/Hz)	Assignment	Spin system	δ(J/Hz)
8c	$[IrCl_2(PhNHNH_2)\{P(OEt)_3\}(AsPh_3)_2]BPh_4$	3299w 3242m 3197m 1597m	ν(NH) $\delta(NH_2)$	6.61 (m) 4.63 (m) 3.58 (m) 1.02 (m)	NH $IrNH_2$ CH_2 CH_3	A	29.3 (s)
9a	$[IrH_2(NH_2NH_2)(PPh_3)_3]BPh_4$	3359w 3298m 3257m 2175w (br)	ν(NH) ν(IrH)	3.92 (m) 2.26 (m) −12.04 (dtd, $J_{H_BH_A} = 5$, $J_{PH_{trans}} = 120$, $J_{PH_{cis}} = 20$) −20.86 (dtd, $J_{H_AH_B} = 5$, $J_{PH_{cis}} = J_{PH_{cis}} = 15$)	$IrNH_2$ NH_2 IrH_B[f] IrH_A	A_2B	δ_A 9.1 δ_B 4.1 $J_{AB} = 15$
9b	$[IrH_2(MeNHNH_2)(PPh_3)_3]BPh_4$	3341w, 3284w 2176w (br)	ν(NH) ν(IrH)	3.70 (br) 1.92 (m, br) 1.58 (d, $J_{HH} = 6$) −12.15 (dtd, $J_{H_BH_A} = 5$, $J_{PH_{trans}} = 120$, $J_{PH_{cis}} = 20$) −20.76 (dtd, $J_{H_AH_B} = 5$, $J_{PH_{cis}} = J_{PH_{cis}} = 17$)	$IrNH_2$ NH CH_3 IrH_B[f] IrH_A	A_2B	δ_A 9.4 δ_B 3.9 $J_{AB} = 12$
10a	$[IrHCl(NH_2NH_2)(PPh_3)_2]BPh_4$	3334m, 3248m 2267m	ν(NH) ν(IrH)	4.38 (m, br) 2.64 (br) −21.42 (t, $J_{PH} = 18$)	$IrNH_2$ NH_2 IrH	A_2	−4.4 (s)
10b	$[IrHCl(MeNHNH_2)(PPh_3)_2]BPh_4$	3269w, 3210w 2245w	ν(NH) ν(IrH)	4.93 (br) 3.70 (br) 2.02 (br) −20.98 (t, $J_{PH} = 17$) 5.14 (d, br)[g] 3.69 (br) 1.97 (d)	$IrNH_2$ NH CH_3 IrH $IrNH_2$ NH CH_3	A_2	−4.6 (s)
10c	$[IrHCl(PhNHNH_2)(PPh_3)_2]BPh_4$	3269m, 3213m 2200w 1601m	ν(NH) ν(IrH) $\delta(NH_2)$	6.05 (t, br) 5.30 (m, br) −20.43 (t, $J_{PH} = 18$)	$IrNH_2$ NH IrH	A_2	−4.4 (s)
11c	$[IrCl_2(PhN{=}NH)\{PPh(OEt)_2\}(PPh_3)_2]BPh_4$			12.49 (d, $J_{PH} = 12$) 3.65 (m) 1.17 (t)[e]	NH CH_2 CH_3	AB_2[h]	δ_A 64.6 δ_B −20.0 $J_{AB} = 22$
11c$_1$	$[IrCl_2(PhN{=}^{15}NH)\{PPh(OEt)_2\}(PPh_3)_2]BPh_4$			12.50 (ddt, $^1J_{^{15}NH} = 66$, $J_{PH} = 12$, $J_{PH} = 2$) 3.71 (m) 1.18 (t)[h]	NH CH_2 CH_3	AB_2X[h] (X = ^{15}N)	δ_A 64.6 δ_B −20.0 $J_{AB} = 21.7$ $J_{AX} = 75.2$ $J_{BX} = 3.6$
11c$_2$	$[IrCl_2(Ph^{15}N{=}NH)\{PPh(OEt)_2\}(PPh_3)_2]BPh_4$			12.50 (dd, $^2J_{^{15}NH} = 4$, $J_{PH} = 12$) 3.71 (m) 1.18 (t)[h]	NH CH_2 CH_3	AB_2[h]	δ_A 64.4 δ_B −20.0 $J_{AB} = 22$
11f	$[IrCl_2(4\text{-}MeC_6H_4N{=}NH)\{PPh(OEt)_2\}$-$(PPh_3)_2]BPh_4$	(342w)	ν(IrCl)	12.28 (d, $J_{PH} = 12$) 3.73 (m) 2.41 (s) 1.19 (t)[h]	NH CH_2 CH_3 *p*-tolyl CH_3 phos	AB_2[h]	δ_A 64.7 δ_B −19.9 $J_{AB} = 22$
12c	$[IrCl_2(PhN{=}NH)\{P(OEt)_3\}(PPh_3)_2]BPh_4$			12.36 (d, $J_{PH} = 12$)[h] 3.74 (qnt) 1.07 (t)	NH CH_2 CH_3	AB_2[h]	δ_A 30.1 δ_B −15.9 $J_{AB} = 26$
12f	$[IrCl_2(4\text{-}MeC_6H_4N{=}NH)\{P(OEt)_3\}$-$(PPh_3)_2]BPh_4$	(338w)	ν(IrCl)	12.14 (d, $J_{PH} = 12$) 3.75 (m) 2.41 (s) 1.09 (t)[h]	NH CH_2 CH_3 *p*-tolyl CH_3 phos	AB_2[h]	δ_A 30.6 δ_B −15.9 $J_{AB} = 26$

Table 1 (*Contd.*)

		IR[a]		^1H NMR[b,c]			$^{31}P-\{^1H\}$ NMR[b,d]
	Compound	ν/cm^{-1}	Assignment	$\delta(J/Hz)$	Assignment	Spin system	$\delta(J/Hz)$
13c	$[IrCl_2(PhN{=}NH)\{PPh(OEt)_2\}(AsPh_3)_2]BPh_4$			12.64 (d,	NH	A	64.6 (s)
				J_{PH} = 12)			
				3.58 (m)	CH_2		
				1.11 (t)	CH_3		
14c	$[IrCl_2(PhN{=}NH)\{P(OEt)_3\}(AsPh_3)_2]BPh_4$			12.90 (d,	NH	A[h]	32.0 (s)
				J_{PH} = 12)			
				3.88 (qnt)	CH_2		
				1.04 (t)[h]	CH_3		
14f	$[IrCl_2(4\text{-}MeC_6H_4N{=}NH)\{P(OEt)_3\}\text{-}(AsPh_3)_2]BPh_4$	(340w)	ν(IrCl)	12.32 (d,	NH	A[i]	32.2 (s)
				J_{PH} = 12)			
				3.61 (qnt)	CH_2		
				2.37 (s)	CH_3 *p*-tolyl		
				0.95 (t)[i]	CH_3 phos		
15c	$[\{IrCl_2[PPh(OEt)_2](PPh_3)_2\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4\text{–}C_6H_4N{=}NH)](BPh_4)_2$			12.55 (d),	NH	AB_2[h]	δ_A 64.7
				12.40 (d)			δ_B −20.0
				(J_{PH} = 12)			J_{AB} = 21.1
				3.72 (m)	CH_2	AB_2	δ_A 64.3
				1.18 (t),	CH_3		δ_B −20.0
				1.15 (t)[h]			J_{AB} = 21.1
15c₁	$[\{IrCl_2[PPh(OEt)_2](PPh_3)_2\}_2(\mu\text{-}4,4'\text{-}H^{15}N{=}NC_6H_4\text{–}C_6H_4N{=}^{15}NH)](BPh_4)_2$			12.55 (dd),	NH	AB_2X[h]	δ_A 64.7
				12.39 (dd)		(X = ^{15}N)	δ_B −19.9
				($J_{^{15}NH}$ = 66,			J_{AB} = 21.1
				J_{PH} = 12)			J_{AX} = 73.3
				3.72 (m)	CH_2		J_{BX} = 3.0
				1.18 (t),	CH_3	AB_2X	δ_A 64.3
				1.14 (t)[h]		(X = ^{15}N)	δ_B −19.9
							J_{AB} = 21.1
							J_{AX} = 75.0
							J_{BX} = 3.0
15f	$[\{IrCl_2[PPh(OEt)_2](PPh_3)_2\}_2\{\mu\text{-}4,4'\text{-}HN{=}N\text{-}(2\text{-}Me)C_6H_3\text{–}C_6H_3(Me\text{-}2)N{=}NH\}](BF_4)_2$			12.16 (d,	NH	AB_2	δ_A 64.4
				J_{PH} = 12)			δ_B −21.6
				3.55 (m)	CH_2		J_{AB} = 22
				2.65 (s)	CH_3 *p*-tolyl		
				1.15 (t)	CH_3 phos		
16c	$[\{IrCl_2\{P(OEt)_3\}(PPh_3)_2\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4\text{–}C_6H_4N{=}NH)](BPh_4)_2$			12.15 (d,	NH	AB_2[h]	δ_A 30.4
				J_{PH} = 12)			δ_B −15.8
				3.76 (qnt)	CH_2		J_{AB} = 26
				1.09 (t)[h]	CH_3		
17c	$[\{IrCl_2\{PPh(OEt)_2\}(AsPh_3)_2\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4\text{–}C_6H_4N{=}NH)](BPh_4)_2$			13.05 (d),	NH	A[h]	65.7 (s)
				12.89 (d)		A	65.3 (s)
				(J_{PH} = 12)			
				3.76 (m)	CH_2		
				1.15 (m)[h]	CH_3		
18c	$[\{IrCl_2\{P(OEt)_3\}(AsPh_3)_2\}_2(\mu\text{-}4,4'\text{-}HN{=}NC_6H_4\text{–}C_6H_4N{=}NH)](BPh_4)_2$			12.97 (d),	NH	A[h]	32.3 (s)
				12.81 (d)		A	31.8 (s)
				(J_{PH} = 12)			
				3.86 (m)	CH_2		
				1.05 (t), 1.02 (t)[h]	CH_3		

[a] In KBr or (polyethylene). [b] In CD_2Cl_2 at 25 °C. [c] Phenyl proton resonances are omitted. [d] Positive shift downfield from 85% H_3PO_4. [e] In C_6D_6. [f] See Fig. 3 in the text. [g] At −30 °C. [h] In $(CD_3)_2CO$. [i] In $CDCl_3$.

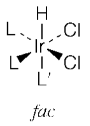
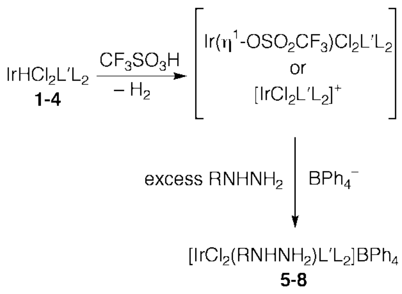


Fig. 1 L = PPh_3 or $AsPh_3$, L′ = $PPh(OEt)_2$ or $P(OEt)_3$.



Scheme 2 L = PPh_3, L′ = $PPh(OEt)_2$ **5a–d**; L = PPh_3, L′ = $P(OEt)_3$ **6a–d**; L = $AsPh_3$, L′ = $PPh(OEt)_2$ **7a,c**; L = $AsPh_3$, L′ = $P(OEt)_3$ **8a–c**; R = H **a**, Me **b**, Ph **c** or $C_6H_4NO_2$-4 **d**.

Hydrazine complexes

Hydrazine complexes $[IrCl_2(RNHNH_2)L'L_2]BPh_4$ **5–8** were prepared by treating the hydride species $IrHCl_2[PPh(OEt)_2]L_2$ and $IrHCl_2[P(OEt)_3]L_2$ first with triflic acid and then with an excess of the appropriate $RNHNH_2$ ligand, as shown in Scheme 2.

The reaction of hydrides **1–4** with CF_3SO_3H proceeds with the evolution of H_2 (^1H NMR signal at δ 4.6)[15] and the probable formation of either the triflate $Ir(\eta^1\text{-}OSO_2CF_3)Cl_2L'L_2$ or the pentacoordinate $[IrCl_2L'L_2]^+$ complex, which were not isolated. Treatment of these intermediates with an excess of the appropriate hydrazine affords the final complexes **5–8**, which were isolated as BPh_4 salts and characterised. It

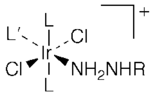
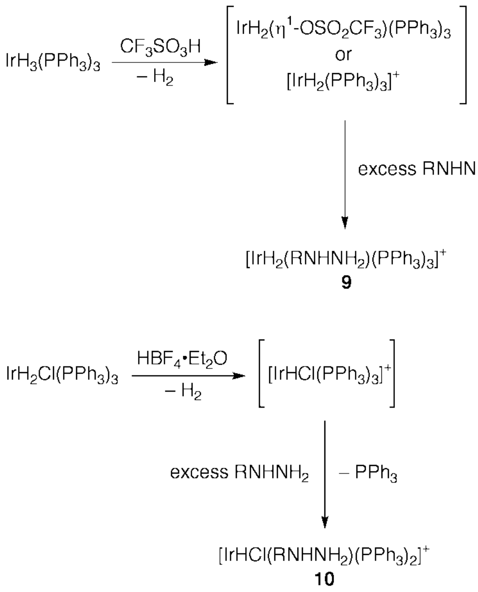


Fig. 2 L = PPh_3 or $AsPh_3$, L′ = $PPh(OEt)_2$ or $P(OEt)_3$.

may be noted that hydrazine complexes can only be obtained from mixed-ligand hydrides **1**–**4**, whereas the use of $IrHCl_2(PPh_3)_3$ or $IrHCl_2(AsPh_3)_3$ as precursors affords only mixtures of products not containing coordinated hydrazine. The nature of the ancillary ligands therefore plays an important role in stabilising the coordination of the hydrazine molecule on the central iridium atom.

Good analytical data were obtained for all hydrazine complexes **5**–**8**, which are white or yellow solids, stable in air and in solutions of polar organic solvents, where they behave as 1 : 1 electrolytes.[16] The spectroscopic data (IR and NMR, see Table 1) support the proposed formulation and allow the geometry in solution to be established. The IR spectra show the characteristic ν(NH) and $\delta(NH_2)$ bands of the hydrazine ligand at 3347–3197 and 1616–1597 cm^{-1}, respectively. The ^1H NMR spectra also confirm the presence of the metal-bonded $RNHNH_2$ ligand, showing slightly broadened NH_2 and NH signals, which were unambiguously assigned by accurate integration and homodecoupling experiments. The ^{13}P-{^1H} NMR spectra of PPh_3 derivatives **5**, **6** show an AB_2 multiplet (Table 1), in accord with the presence of two magnetically equivalent phosphines which are different from the third. Only one singlet appears in the spectra of $AsPh_3$ derivatives **7**, **8**. Furthermore, the far-IR spectra show only one ν(IrCl) band at 338–327 cm^{-1}, indicating the presence of two Cl^- ligands in a mutually *trans* position. Although caution should be used with far-IR data, a *mer-trans* geometry of the type shown in Fig. 2 may be proposed for our hydrazine derivatives **5**–**8**.

These results prompted us to extend the study to other hydrides, in order to test the reaction for the synthesis of other hydrazine derivatives. Results show that, whereas monohydrides $IrHCl_2(PPh)_3$ and $IrHCl_2(AsPh_3)_3$ do not afford hydrazine complexes, the trihydride $IrH_3(PPh_3)_3$ reacts first with triflic acid and then with an excess of the appropriate hydrazine, to give hydride–hydrazine cations $[IrH_2(RNHNH_2)(PPh_3)_3]^+$ **9** which were isolated as BPh_3 salts and characterised (Scheme 3).



Scheme 3 R = H **a**, Me **b** or Ph **c**.

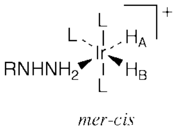


Fig. 3 L = PPh_3.

Surprisingly, no hydrazine complexes were obtained by reacting dihydride species $IrH_2Cl(PPh_3)_3$ first with CF_3SO_3H and then with $RNHNH_2$. However, when $IrH_2Cl(PPh_3)_3$ was treated with $HBF_4{\cdot}Et_2O$ instead of CF_3SO_3H and then with $RNHNH_2$, pentacoordinate hydrazine complexes $[IrHCl(RNHNH_2)(PPh_3)_2]BPh_4$ **10** were obtained in good yield after precipitation with BPh_4 salts (Scheme 3).

The reaction of $IrH_3(PPh_3)_3$ with triflic acid proceeds with the evolution of H_2 (by ^1H NMR) and the probable formation of either η^1-OSO_2CF_3 or pentacoordinate $[IrH_2(PPh_3)_3]^+$ intermediates which, on treatment with $RNHNH_2$, afford the final hydrazine complexes **9**. Evolution of H_2 was also observed in the reaction of $IrH_2Cl(PPh_3)_3$ with $HBF_4{\cdot}Et_2O$, giving the probable intermediate $[IrHCl(PPh_3)_3]^+$, which reacts with hydrazine to give final complex **10**. The reaction proceeds with loss of one PPh_3 ligand, affording the pentacoordinate bis(phosphino) $[IrHCl(RNHNH_2)(PPh_3)_2]BPh_4$ derivative **10**.

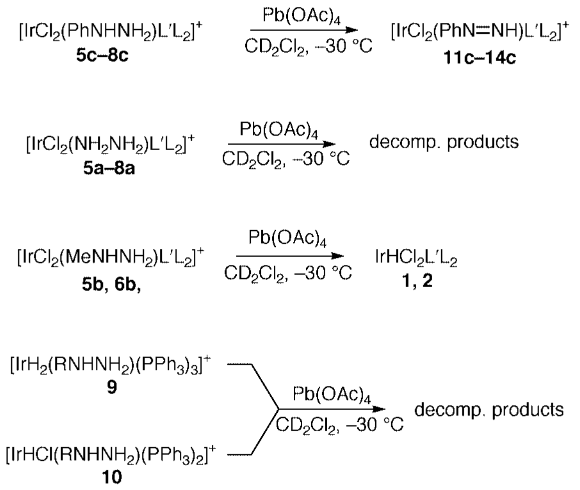
Good analytical data were obtained for both complexes **9** and **10**, which are all air-stable white solids, diamagnetic, and 1 : 1 electrolytes.[16] The IR and NMR data are listed in Table 1 and confirm the proposed formulation. In particular, the ^1H NMR spectra of $[IrH_2(RNHNH_2)(PPh_3)_3]BPh_4$ derivatives **9** display two sets of signals in the low frequency region, each appearing as a doublet of triplets of doublets, due to the coupling of two chemically inequivalent hydride ligands, H_A and H_B (Fig. 3), with the phosphorus nuclei of the phosphine ligands. The ^{31}P-{^1H} NMR spectra of **9** show A_2B multiplets, in agreement with two magnetically equivalent phosphines, different from the third. Furthermore, the J_{PH} values of hydrides H_A and H_B are quite different, and the value of 120 Hz observed in one case, compared with the other two, indicates the mutually *trans* position of this hydride with one phosphine ligand. On these bases, a *mer-cis* geometry of the type shown in Fig. 3 may be proposed for our complexes **9**.

The ^1H NMR spectra of $[IrHCl(RNHNH_2)(PPh_3)_2]BPh_4$ **10** show a triplet at δ *ca.* −21 in the low frequency region, due to coupling of the hydride ligand with two chemically equivalent phosphorus nuclei. The equivalence of the two PPh_3 ligands is confirmed by the ^{31}P-{^1H} NMR spectra which, between 30 and −90 °C, show only one singlet. However, the spectroscopic data alone do not allow us to unambiguously assign a geometry for these pentacoordinate hydrazine complexes and, in the absence of an X-ray structure, no geometrical assignment can be made.

Oxidation reactions

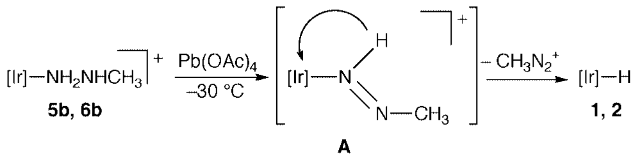
The oxidation reactions of hydrazine complexes **5**–**10** with $Pb(OAc)_4$ were studied extensively. The results are summarised in Scheme 4.

Phenylhydrazine cations $[IrCl_2(PhNHNH_2)L'L_2]^+$ **5c**–**8c** react with $Pb(OAc)_4$ at −30 °C to give the corresponding phenyldiazene derivatives $[IrCl_2(PhN{=}NH)L'L_2]^+$ **11c**–**14c**, which were isolated as yellow solids and characterised. Support for their formulation comes from spectroscopic data and by comparisons with similar complexes prepared by reacting hydrides $IrHCl_2L'L_2$ **1**–**4** with aryldiazonium cations (see below). The related $[IrCl_2(NH_2NH_2)L'L_2]^+$ derivatives **5a**–**8a**, react with $Pb(OAc)_4$ but do not yield any diazene derivatives as the solids recovered from the reaction mixture only contain decomposition products. Hydride–hydrazine complexes **9** and **10** also give only decomposition products when treated with $Pb(OAc)_4$, and no traces of diazene species could be detected. Surprisingly, the reaction of methylhydrazine complexes $[IrCl_2(MeNHNH_2)L'L_2]BPh_4$ **5b**, **6b** with $Pb(OAc)_4$ at low temperature (−30 °C) proceeds to give the hydrides $IrHCl_2[PPh(OEt)_2](PPh_3)_2$ or



Scheme 4 L′ = PPh(OEt)$_2$ or P(OEt)$_3$; L = PPh$_3$ or AsPh$_3$; R = H or Me.

IrHCl$_2$[P(OEt)$_3$](PPh$_3$)$_2$ as final products. The formation of a hydride species by oxidation of a methylhydrazine with Pb(OAc)$_4$ is rather unexpected, and may be explained on the basis of the path in Scheme 5, which involves methyldiazene {[Ir]–NH=NMe}$^+$ **A** as an intermediate. The methyldiazene ligand may be unstable on the iridium centre and decompose, transferring the hydride hydrogen atom to the metal and liberating the unstable methyldiazonium MeN$_2^+$ species. This mechanism may seem inappropriate, since aryldiazonium cations are generally inserted into the metal–hydride bond to give aryldiazine species,[1,2] whereas the path in Scheme 5 proposes a reaction which is the reverse of an insertion. However, in our case, an aliphatic diazene is involved, the properties of which are very little known[17,18] when compared with those of the related aryldiazene.[1,2] Furthermore, the precedent[19] for the formation of the hydride species ReH(CO)$_3$(PPh$_3$)$_2$ by the reaction of the 1,2-diazene complex [Re(CO)$_3$(NH=NH)(PPh$_3$)$_2$]$^+$ with base partly supports the proposed mechanism.



Scheme 5 [Ir] = IrCl$_2$PL$_2$.

These results on the reactivity of hydrazine complexes of iridium show that Pb(OAc)$_4$ may be a selective oxidant of the RNHNH$_2$ molecule, but only in a few cases can the related diazene complexes be isolated. Except in the phenyl PhNHNH$_2$ species, in fact, the oxidation reactions of all hydrazine and methylhydrazine complexes always give rise to products which do not contain the diazene ligand.

Aryldiazene derivatives

The formation of aryldiazene complexes **11c**–**14c** by oxidation of arylhydrazine derivatives of iridium(III) prompted us to study the reaction of hydrides IrHCl$_2$L′L$_2$ **1**–**4** with aryldiazonium cations, in order to test an alternative synthesis of {[Ir]–ArN=NH}$^+$ derivatives. The results are summarised in Scheme 6.

Both mono- ArN$_2^+$ and bis- [N$_2$Ar–ArN$_2$]$^{2+}$ aryldiazonium cations react with hydrides **1**–**4** to give aryldiazene complexes [IrCl$_2$(ArN=NH)L′L$_2$]$^+$ **11**–**14** and [{IrCl$_2$L′L$_2$}$_2$(μ-NH=NAr–ArN=NH)]$^{2+}$ **15**–**18**, which were isolated as BPh$_4$ salts and characterised. Crucial for the successful synthesis of aryldiazene complexes is an exact stoichiometric ratio between the reagents and a low temperature at the start (−80 °C) and during the course (0 °C) of the reaction. Otherwise, large amounts of decomposition products or oily substances are found in the final reaction products.

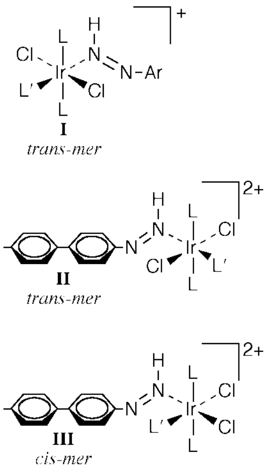
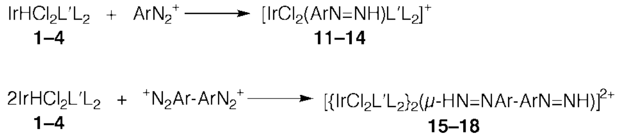


Fig. 4 L = PPh$_3$ or AsPh$_3$, L′ = PPh(OEt)$_2$ or P(OEt)$_3$.



Scheme 6 L = PPh$_3$, L′ = PPh(OEt)$_2$ **11**, **15** (**c**,**f**); L = PPh$_3$, L′ = P(OEt)$_3$ **12** (**c**–**f**), **16c**; L = AsPh$_3$, L′ = PPh(OEt)$_2$ **13c**, **17c**; L = AsPh$_3$, L′ = P(OEt)$_3$ **14** (**c**–**f**), **18c**; Ar = Ph **c** or C$_6$H$_4$Me-4 **f**; Ar–Ar = 4,4′-C$_6$H$_4$–C$_6$H$_4$ **c** or 4,4′-(2-Me)C$_6$H$_3$–C$_6$H$_3$(Me-2) **f**.

Complexes **11**–**18** are yellow or orange solids, stable in air and in solutions of polar organic solvents, where they behave as 1 : 1 or 2 : 1 electrolytes.[16] The analytical and spectroscopic data (Table 1) support the proposed formulation. Diagnostic for the presence of the diazene ligand in both mono- and bi-nuclear complexes is the high-frequency ^{1}H NMR multiplet of the NH proton at δ 13.05–12.14, which is split into a doublet of multiplets in labelled compounds **11c$_1$**, **11c$_2$**, **15c$_1$**. The values for both $^1J_{^{15}\mathrm{NH}}$ and $^2J_{^{15}\mathrm{NH}}$, 66 and 4 Hz, respectively, were also determined[1,7,20] and agree with the proposed formulation.

It may also be noted that the spectra of three binuclear complexes, *i.e.* **15c**, **17c** and **18c**, show two sets of signals in the NH region, which are each split into one doublet of multiplets (**15c$_1$**), in agreement with the presence of two diazene species. As the ^{31}P spectra of **15c**, **17c** and **18c** also show two sets of signals, the existence of two isomers of types **II** and **III** (Fig. 4) may be invoked to explain the data of the three compounds. Instead, only one isomer with *trans-mer* geometry, of types **I** or **II** can be proposed for all the other mono- and bi-nuclear aryldiazene complexes **11**–**18**, except **15c**, **17c** and **18c**. The ^{31}P{^{1}H} NMR spectra show only one AB$_2$ multiplet for the PPh$_3$ derivatives and a sharp singlet for the AsPh$_3$ ones, whereas the ^{1}H NMR spectra only show one signal for the diazene NH proton. Furthermore, the far-IR spectra are consistent with the presence of two Cl$^-$ ligands in a mutually *trans* position showing only one ν(IrCl) band at 342–338 cm^{-1}, in agreement with proposed geometries **I** and **II**.

Lastly, it may be noted that the far-IR spectra of the three compounds **15c**, **17c** and **18c** show the presence of more than one ν(IrCl) band (which partly overlap), in agreement with the existence of a mixture of isomers of types **II** and **III** (Fig. 4) for each compound.

Conclusions

This contribution reports data on a series of hydrazine complexes of iridium of the type [IrCl$_2$(RNHNH$_2$)L′L$_2$]-

BPh_4, which may be prepared using the mixed-ligand hydrides $IrHCl_2[PPh(OEt)_2]L_2$ and $IrHCl_2[P(OEt)_3]L_2$ as precursors. Hydride–hydrazine derivatives $[IrH_2(RNHNH_2)(PPh_3)_3]BPh_4$ and $[IrHCl(RNHNH_2(PPh_3)_2]BPh_4$ were also prepared by an analogous procedure. Among the properties shown by these hydrazine complexes is selective oxidation of the arylhydrazine $RNHNH_2$ ligand, giving the corresponding aryldiazene *complexes* $[IrCl_2(ArN{=}NH)L'L_2]BPh_4$. The same aryldiazene species $[IrCl_2(ArN{=}NH)L'L_2]BPh_4$ may also be obtained through the insertion of an aryldiazonium cation into the Ir–H bond of hydrides $IrHCl_2L'L_2$. This reaction also allows the binuclear complexes $[\{IrCl_2L'L_2\}_2(\mu\text{-}HN{=}NAr\text{–}ArN{=}NH)](BPh_4)_2$ containing the bis(aryldiazene) bridging ligand to be prepared.

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