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 $[\{IrCl_2L'L_2\}_2(\mu-HN=NAr-ArN=NH)](BPh_4)_2$ **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 $IrCl_3\cdot3H_2O$ 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) $[N_2Ar-ArN_2](BF_4)_2$ [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 $H_2NAr-ArNH_2$ with $NaNO_2$, as described in the literature for common mono-diazonium salts.[11] Labelled diazonium tetrafluoroborates $[PhN\equiv^{15}N]BF_4$ and $[4,4'-^{15}N\equiv NC_6H_4-C_6H_4N\equiv^{15}N](BF_4)_2$ were prepared from $Na^{15}NO_2$ (99% enriched, CIL) and the appropriate amine. Alternatively, the $[Ph^{15}N\equiv N]BF_4$ 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-$\{^1H\}$ 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.

Synthesis of complexes

Hydrides *mer*-IrHCl$_2$(PPh$_3$)$_3$, *mer*-IrHCl$_2$(AsPh$_3$)$_3$, IrH$_2$Cl-(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$_2$-IrO$_2$P$_3$ 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$_2$IrO$_3$P$_3$ 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$_2$Cl$_2$-IrO$_2$P 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$_2$Cl$_2$IrO$_3$P 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$_6$H$_4$NO$_2$-4 d). To a solution of the appropriate hydride (0.50 mmol) in 20 cm^3 of CH$_2$Cl$_2$, cooled to −80 °C, was added an equimolar amount of CF$_3$SO$_3$H (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$_2$NH$_2$, 5 mmol for 4-NO$_2$C$_6$H$_4$NHNH$_2$) 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$_2$Cl$_2$ (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$_2$IrN$_2$O$_2$P$_3$ **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$_2$IrN$_2$O$_2$P$_3$ **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$_2$IrN$_2$O$_2$P$_3$ **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$_2$IrN$_3$O$_4$P$_3$ **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$_2$IrN$_2$O$_3$P$_3$ **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$_2$IrN$_2$O$_3$P$_3$ **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$_2$IrN$_3$O$_5$P$_3$ **6d** requires C, 60.6; H, 5.1; N, 2.95; Cl, 5.0%).

[IrCl$_2$(NH$_2$NH$_2$){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$_3$SO$_3$H (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$_2$NH$_2$ (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$_2$Cl$_2$ (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$_2$IrN$_2$O$_3$P$_3$ requires C, 60.7; H, 5.3; N, 2.15; Cl, 5.4%).

[IrCl$_2$(Me$_2$NNH$_2$){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$_2$NNH$_2$ (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$_2$IrN$_2$O$_3$P$_3$ 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$_2$BCl$_2$IrN$_2$O$_2$P **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$_2$BCl$_2$IrN$_2$O$_2$P **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$_2$-BCl$_2$IrN$_2$O$_2$P **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$_2$BCl$_2$IrN$_2$O$_3$P **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$_2$BCl$_2$IrN$_2$O$_3$P **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$_3$SO$_3$H (13 μL, 0.153 mmol) and the reaction mixture brought to room temperature. After the addition of 5 cm^3 of CH$_2$Cl$_2$, 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$_2$Cl$_2$ (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$_2$P$_3$ **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$_2$P$_3$ **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$_2$Cl(PPh$_3$)$_3$ (0.102 g, 0.1 mmol) in 10 cm^3 of CH$_2$Cl$_2$, cooled to −80 °C, was added an equimolar amount of HBF$_4$·Et$_2$O (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$_2$Cl$_2$ (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$_2$P$_2$ **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$_2$P$_2$ **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$_2$P$_2$ **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.
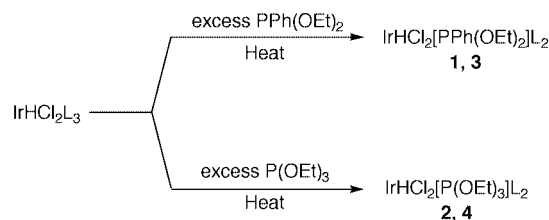
Scheme 1 L = PPh$_3$ **1, 2** or AsPh$_3$ **3, 4**.

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

	Compound	IR[a]		¹H NMR[b,c]			³¹P-{¹H} NMR[b,d]
		ν/cm⁻¹	Assignment	δ(J/Hz)	Assignment	Spin system	δ(J/Hz)
1	IrHCl₂[PPh(OEt)₂](PPh₃)₂	2116w	ν(IrH)	3.84 (m), 3.51 (m)	CH₂	AB₂[e]	δ_A 102.0
		(333w)	ν(IrCl)	0.98 (t)	CH₃		δ_B −2.4
		(326w)		−10.49 (dt,	IrH		J_{AB} = 16
				$J_{PH_{trans}}$ = 220,			
				$J_{PH_{cis}}$ = 15)[e]			
2	IrHCl₂[P(OEt)₃](PPh₃)₂	2073w	ν(IrH)	3.58 (qnt)	CH₂	AB₂[e]	δ_A 79.9
				0.92 (t)	CH₃		δ_B −1.66
				−10.38 (dt,	IrH		J_{AB} = 22
				$J_{PH_{trans}}$ = 262,			
				$J_{PH_{cis}}$ = 16)[e]			
3	IrHCl₂[PPh(OEt)₂](AsPh₃)₂	2065w	ν(IrH)	3.92 (m)	CH₂	A[e]	82.0 (s)
				3.49 (m)			
				0.99 (t)	CH₃		
				−9.80 (d,	IrH		
				J_{PH} = 225)[e]			
4	IrHCl₂[P(OEt)₃](AsPh₃)₂	2051w	ν(IrH)	3.70 (qnt)	CH₂	A[e]	85.6 (s)
				0.92 (t)	CH₃		
				−9.67 (d,	IrH		
				J_{PH} = 265)[e]			
5a	[IrCl₂(NH₂NH₂){PPh(OEt)₂}(PPh₃)₂]BPh₄	3342w	ν(NH)	4.22 (br)	IrNH₂	AB₂	δ_A 63.4
		3276m		3.45 (m)	CH₂		δ_B −22.6
		3263w		3.07 (m, br)	NH₂		J_{AB} = 22
		3226w		1.18 (t)	CH₃		
		(338m)	ν(IrCl)				
5b	[IrCl₂(MeNHNH₂){PPh(OEt)₂}(PPh₃)₂]BPh₄	3329w	ν(NH)	3.98 (br)	IrNH₂	AB₂	δ_A 62.2
		3248m		3.80 (m)	NH		δ_B −22.2
		3240w		3.38 (m)	CH₂		J_{AB} = 21
				1.56 (d, J_{HH} = 8)	CH₃ hydraz		
				1.07 (t)	CH₃ phos		
5c	[IrCl₂(PhNHNH₂){PPh(OEt)₂}(PPh₃)₂]BPh₄	3302w	ν(NH)	6.49 (br)	NH	AB₂	δ_A 61.1
		3241m		4.57 (br)	IrNH₂		δ_B −22.7
		3197w		3.47 (m)	CH₂		J_{AB} = 22
		1604m	δ(NH₂)	1.13 (t)	CH₃		
5d	[IrCl₂(4-NO₂C₆H₄NHNH₂){PPh(OEt)₂}-(PPh₃)₂]BPh₄	3311w	ν(NH)	4.49 (br)	IrNH₂	AB₂	δ_A 59.9
		3230m		3.45 (m)	CH₂		δ_B −23.2
		1602m	δ(NH₂)	1.09 (t)	CH₃		J_{AB} = 22
6a	[IrCl₂(NH₂NH₂){P(OEt)₃}(PPh₃)₂]BPh₄	3342m	ν(NH)	4.12 (m)	IrNH₂	AB₂	δ_A 30.8
		3270m		3.43 (qnt)	CH₂		δ_B −18.7
		3250(sh)		3.08 (br)	NH₂		J_{AB} = 26
		(327w)	ν(IrCl)	0.99 (t)	CH₃		
6b	[IrCl₂(MeNHNH₂){P(OEt)₃}(PPh₃)₂]BPh₄	3302w	ν(NH)	3.94 (m)	IrNH₂	AB₂	δ_A 28.7
		3256m		3.80 (m)	NH		δ_B −18.0
		3197m		3.42 (qnt)	CH₂		J_{AB} = 26
				1.61 (d, J_{HH} = 4)	CH₃ hydraz		
				0.99 (t)	CH₃ phos		
6c	[IrCl₂(PhNHNH₂){P(OEt)₃}(PPh₃)₂]BPh₄	3317m	ν(NH)	6.40 (m)	NH	AB₂	δ_A 28.1
		3257m		4.45 (m)	IrNH₂		δ_B −18.9
		3197w		3.44 (qnt)	CH₂		J_{AB} = 26
		1601m	δ(NH₂)	1.00 (t)	CH₃		
6d	[IrCl₂(4-NO₂C₆H₄NHNH₂){P(OEt)₃}-(PPh₃)₂]BPh₄	3282m	ν(NH)	4.40 (m)	IrNH₂	AB₂	δ_A 26.0
		3227w		3.47 (qnt)	CH₂		δ_B −19.5
		1602m	δ(NH₂)	1.01 (t)	CH₃		J_{AB} = 26
6e	[IrCl₂(Me₂NNH₂){P(OEt)₃}(PPh₃)₂]BPh₄	3310w	ν(NH)	4.12 (br)	IrNH₂	AB₂	δ_A 21.5
		3233m		3.55 (qnt)	CH₂		δ_B −17.4
		1616m	δ(NH₂)	2.39 (s)	CH₃ hydraz		J_{AB} = 20
				1.06 (t)	CH₃ phos		
7a	[IrCl₂(NH₂NH₂){PPh(OEt)₂}(AsPh₃)₂]BPh₄	3340m	ν(NH)	4.45 (m)	IrNH₂	A	63.6 (s)
		3271m		3.48 (qnt)	CH₂		
		3263w		3.29 (m)	NH₂		
		3223m		1.01 (t)	CH₃		
7c	[IrCl₂(PhNHNH₂){PPh(OEt)₂}(AsPh₃)₂]BPh₄	3299m	ν(NH)	6.64 (m)	NH	A	61.4 (s)
		3242m		4.75 (t, br)	IrNH₂		
		3197w		3.54 (qnt)	CH₂		
		1597m	δ(NH₂)	1.10 (t)	CH₃		
		(332w)	ν(IrCl)				
8a	[IrCl₂(NH₂NH₂){P(OEt)₃}(AsPh₃)₂]BPh₄	3347w	ν(NH)	4.39 (m)	IrNH₂	A	31.6 (2)
		3263m		3.57 (m)	CH₂		
		3230m		3.36 (m)	NH₂		
		3158w		1.00 (t)	CH₃		
8b	[IrCl₂(MeNHNH₂){P(OEt)₃}(AsPh₃)₂]BPh₄	3308w	ν(NH)	4.10 (m)	NH	A	30.1 (s)
		3244m		4.21 (m)	IrNH₂		
		3202w		3.58 (qnt)	CH₂		
		1597m	δ(NH₂)	1.73 (d,	CH₃ hydraz		
		(335w)	ν(IrCl)	J_{HH} = 6)			
				1.00 (t)	CH₃ phos		

Table 1 (*Contd.*)

Compound	IR[a] ν/cm⁻¹	Assignment	¹H NMR[b,c] δ(J/Hz)	Assignment	Spin system	³¹P-{¹H} NMR[b,d] δ(J/Hz)
8c [IrCl₂(PhNHNH₂){P(OEt)₃}(AsPh₃)₂]BPh₄	3299w 3242m 3197m 1597m	ν(NH) δ(NH₂)	6.61 (m) 4.63 (m) 3.58 (m) 1.02 (m)	NH IrNH₂ CH₂ CH₃	A	29.3 (s)
9a [IrH₂(NH₂NH₂)(PPh₃)₃]BPh₄	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)	IrNH₂ NH₂ IrH$_B$[f] IrH$_A$	A₂B	δ_A 9.1 δ_B 4.1 J_{AB} = 15
9b [IrH₂(MeNHNH₂)(PPh₃)₃]BPh₄	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)	IrNH₂ NH CH₃ IrH$_B$[f] IrH$_A$	A₂B	δ_A 9.4 δ_B 3.9 J_{AB} = 12
10a [IrHCl(NH₂NH₂)(PPh₃)₂]BPh₄	3334m, 3248m 2267m	ν(NH) ν(IrH)	4.38 (m, br) 2.64 (br) −21.42 (t, J_{PH} = 18)	IrNH₂ NH₂ IrH	A₂	−4.4 (s)
10b [IrHCl(MeNHNH₂)(PPh₃)₂]BPh₄	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)	IrNH₂ NH CH₃ IrH IrNH₂ NH CH₃	A₂	−4.6 (s)
10c [IrHCl(PhNHNH₂)(PPh₃)₂]BPh₄	3269m, 3213m 2200w 1601m	ν(NH) ν(IrH) δ(NH₂)	6.05 (t, br) 5.30 (m, br) −20.43 (t, J_{PH} = 18)	IrNH₂ NH IrH	A₂	−4.4 (s)
11c [IrCl₂(PhN=NH){PPh(OEt)₂}(PPh₃)₂]BPh₄			12.49 (d, J_{PH} = 12) 3.65 (m) 1.17 (t)[e]	NH CH₂ CH₃	AB₂[h]	δ_A 64.6 δ_B −20.0 J_{AB} = 22
11c₁ [IrCl₂(PhN=¹⁵NH){PPh(OEt)₂}(PPh₃)₂]BPh₄			12.50 (ddt, ¹$J_{¹⁵NH}$ = 66, J_{PH} = 12, J_{PH} = 2) 3.71 (m) 1.18 (t)[h]	NH CH₂ CH₃	AB₂X[h] (X = ¹⁵N)	δ_A 64.6 δ_B −20.0 J_{AB} = 21.7 J_{AX} = 75.2 J_{BX} = 3.6
11c₂ [IrCl₂(Ph¹⁵N=NH){PPh(OEt)₂}(PPh₃)₂]BPh₄			12.50 (dd, ²$J_{¹⁵NH}$ = 4, J_{PH} = 12) 3.71 (m) 1.18 (t)[h]	NH CH₂ CH₃	AB₂[h]	δ_A 64.4 δ_B −20.0 J_{AB} = 22
11f [IrCl₂(4-MeC₆H₄N=NH){PPh(OEt)₂}-(PPh₃)₂]BPh₄	(342w)	ν(IrCl)	12.28 (d, J_{PH} = 12) 3.73 (m) 2.41 (s) 1.19 (t)[h]	NH CH₂ CH₃ p-tolyl CH₃ phos	AB₂[h]	δ_A 64.7 δ_B −19.9 J_{AB} = 22
12c [IrCl₂(PhN=NH){P(OEt)₃}(PPh₃)₂]BPh₄			12.36 (d, J_{PH} = 12)[h] 3.74 (qnt) 1.07 (t)	NH CH₂ CH₃	AB₂[h]	δ_A 30.1 δ_B −15.9 J_{AB} = 26
12f [IrCl₂(4-MeC₆H₄N=NH){P(OEt)₃}-(PPh₃)₂]BPh₄	(338w)	ν(IrCl)	12.14 (d, J_{PH} = 12) 3.75 (m) 2.41 (s) 1.09 (t)[h]	NH CH₂ CH₃ p-tolyl CH₃ phos	AB₂[h]	δ_A 30.6 δ_B −15.9 J_{AB} = 26

Table 1 (*Contd.*)

| Compound	IR[a] ν/cm^{-1}	Assignment	$^1\text{H NMR}^{b,c}$ $\delta(J/\text{Hz})$	Assignment	Spin system	$^{31}\text{P-}\{^1\text{H}\}$ NMR[b,d] $\delta(J/\text{Hz})$
13c $[\text{IrCl}_2(\text{PhN=NH})\{\text{PPh}(\text{OEt})_2\}(\text{AsPh}_3)_2]\text{BPh}_4$			12.64 (d, $J_{\text{PH}} = 12$)	NH	A	64.6 (s)
			3.58 (m)	CH$_2$		
			1.11 (t)	CH$_3$		
14c $[\text{IrCl}_2(\text{PhN=NH})\{\text{P}(\text{OEt})_3\}(\text{AsPh}_3)_2]\text{BPh}_4$			12.90 (d, $J_{\text{PH}} = 12$)	NH	A[h]	32.0 (s)
			3.88 (qnt)	CH$_2$		
			1.04 (t)[h]	CH$_3$		
14f $[\text{IrCl}_2(4\text{-MeC}_6\text{H}_4\text{N=NH})\{\text{P}(\text{OEt})_3\}$-$(\text{AsPh}_3)_2]\text{BPh}_4$	(340w)	$\nu(\text{IrCl})$	12.32 (d, $J_{\text{PH}} = 12$)	NH	A[i]	32.2 (s)
			3.61 (qnt)	CH$_2$		
			2.37 (s)	CH$_3$ p-tolyl		
			0.95 (t)[i]	CH$_3$ phos		
15c $[\{\text{IrCl}_2[\text{PPh}(\text{OEt})_2](\text{PPh}_3)_2\}_2(\mu\text{-}4,4'\text{-}$ HN=NC$_6$H$_4$–C$_6$H$_4$N=NH)](BPh$_4$)$_2$			12.55 (d), 12.40 (d) ($J_{\text{PH}} = 12$)	NH	AB$_2$[h]	δ_A 64.7 δ_B -20.0 $J_{\text{AB}} = 21.1$
			3.72 (m)	CH$_2$	AB$_2$	δ_A 64.3
			1.18 (t), 1.15 (t)[h]	CH$_3$		δ_B -20.0 $J_{\text{AB}} = 21.1$
15c$_1$ $[\{\text{IrCl}_2[\text{PPh}(\text{OEt})_2](\text{PPh}_3)_2\}_2(\mu\text{-}4,4'\text{-}$ H^{15}N=NC$_6$H$_4$–C$_6$H$_4$N=^{15}NH)](BPh$_4$)$_2$			12.55 (dd), 12.39 (dd) ($J_{^{15}\text{NH}} = 66$, $J_{\text{PH}} = 12$)	NH	AB$_2$X[h] (X = ^{15}N)	δ_A 64.7 δ_B -19.9 $J_{\text{AB}} = 21.1$ $J_{\text{AX}} = 73.3$ $J_{\text{BX}} = 3.0$
			3.72 (m)	CH$_2$		
			1.18 (t), 1.14 (t)[h]	CH$_3$	AB$_2$X (X = ^{15}N)	δ_A 64.3 δ_B -19.9 $J_{\text{AB}} = 21.1$ $J_{\text{AX}} = 75.0$ $J_{\text{BX}} = 3.0$
15f $[\{\text{IrCl}_2[\text{PPh}(\text{OEt})_2](\text{PPh}_3)_2\}_2\{\mu\text{-}4,4'\text{-HN=N-}$ (2-Me)C$_6$H$_3$–C$_6$H$_3$(Me-2)N=NH\}](BF$_4$)$_2$			12.16 (d, $J_{\text{PH}} = 12$)	NH	AB$_2$	δ_A 64.4 δ_B -21.6 $J_{\text{AB}} = 22$
			3.55 (m)	CH$_2$		
			2.65 (s)	CH$_3$ p-tolyl		
			1.15 (t)	CH$_3$ phos		
16c $[\{\text{IrCl}_2\{\text{P}(\text{OEt})_3\}(\text{PPh}_3)_2\}_2(\mu\text{-}4,4'\text{-}$ HN=NC$_6$H$_4$–C$_6$H$_4$N=NH)](BPh$_4$)$_2$			12.15 (d, $J_{\text{PH}} = 12$)	NH	AB$_2$[h]	δ_A 30.4 δ_B -15.8 $J_{\text{AB}} = 26$
			3.76 (qnt)	CH$_2$		
			1.09 (t)[h]	CH$_3$		
17c $[\{\text{IrCl}_2\{\text{PPh}(\text{OEt})_2\}(\text{AsPh}_3)_2\}_2(\mu\text{-}4,4'\text{-}$ HN=NC$_6$H$_4$–C$_6$H$_4$N=NH)](BPh$_4$)$_2$			13.05 (d), 12.89 (d) ($J_{\text{PH}} = 12$)	NH	A[h] A	65.7 (s) 65.3 (s)
			3.76 (m)	CH$_2$		
			1.15 (m)[h]	CH$_3$		
18c $[\{\text{IrCl}_2\{\text{P}(\text{OEt})_3\}(\text{AsPh}_3)_2\}_2(\mu\text{-}4,4'\text{-}$ HN=NC$_6$H$_4$–C$_6$H$_4$N=NH)](BPh$_4$)$_2$			12.97 (d), 12.81 (d) ($J_{\text{PH}} = 12$)	NH	A[h] A	32.3 (s) 31.8 (s)
			3.86 (m)	CH$_2$		
			1.05 (t), 1.02 (t)[h]	CH$_3$		

[a] In KBr or (polyethylene). [b] In CD$_2$Cl$_2$ at 25 °C. [c] Phenyl proton resonances are omitted. [d] Positive shift downfield from 85% H$_3$PO$_4$. [e] In C$_6$D$_6$. [f] See Fig. 3 in the text. [g] At -30 °C. [h] In (CD$_3$)$_2$CO. [i] In CDCl$_3$.
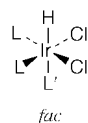
Fig. 1 L = PPh$_3$ or AsPh$_3$, L′ = PPh(OEt)$_2$ or P(OEt)$_3$.

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$_3$SO$_3$H proceeds with the evolution of H$_2$ (¹H NMR signal at δ 4.6)[15] and the probable formation of either the triflate Ir(η^1-OSO$_2$CF$_3$)-Cl$_2$L′L$_2$ or the pentacoordinate [IrCl$_2$L′L$_2$]$^+$ complex, which
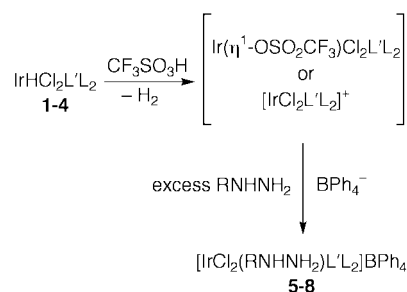
Scheme 2 L = PPh$_3$, L′ = PPh(OEt)$_2$ **5a–d**; L = PPh$_3$, L′ = P(OEt)$_3$ **6a–d**; L = AsPh$_3$, L′ = PPh(OEt)$_2$ **7a,c**; L = AsPh$_3$, L′ = P(OEt)$_3$ **8a–c**; R = H **a**, Me **b**, Ph **c** or C$_6$H$_4$NO$_2$-4 **d**.

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
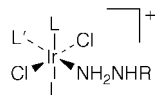
Fig. 2   L = PPh$_3$ or AsPh$_3$, L' = PPh(OEt)$_2$ or P(OEt)$_3$.

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 δ(NH$_2$) bands of the hydrazine ligand at 3347–3197 and 1616–1597 cm^{-1}, respectively. The ^{1}H 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-{^{1}H} 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$_3$)$_3$ 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).
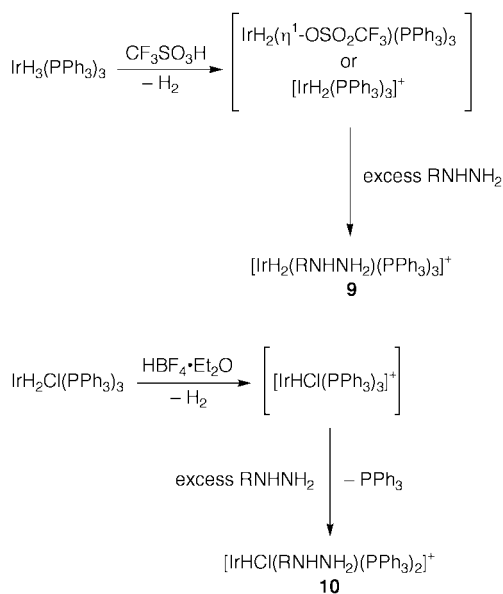
Scheme 3   R = H **a**, Me **b** or Ph **c**.

Surprisingly, no hydrazine complexes were obtained by reacting dihydride species IrH$_2$Cl(PPh$_3$)$_3$ first with CF$_3$SO$_3$H and then with RNHNH$_2$. However, when IrH$_2$Cl(PPh$_3$)$_3$ was treated with

mer-cis
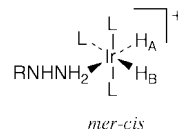
Fig. 3   L = PPh$_3$.

HBF$_4$·Et$_2$O instead of CF$_3$SO$_3$H 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 ^{1}H NMR) and the probable formation of either η^1-OSO$_2$CF$_3$ 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$_2$Cl(PPh$_3$)$_3$ with HBF$_4$·Et$_2$O, 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 ^{1}H 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-{^{1}H} NMR spectra of **9** show A$_2$B 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 ^{1}H 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-{^{1}H} 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$_2$L'L$_2$ **1–4** with aryldiazonium cations (see below). The related [IrCl$_2$(NH$_2$NH$_2$)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
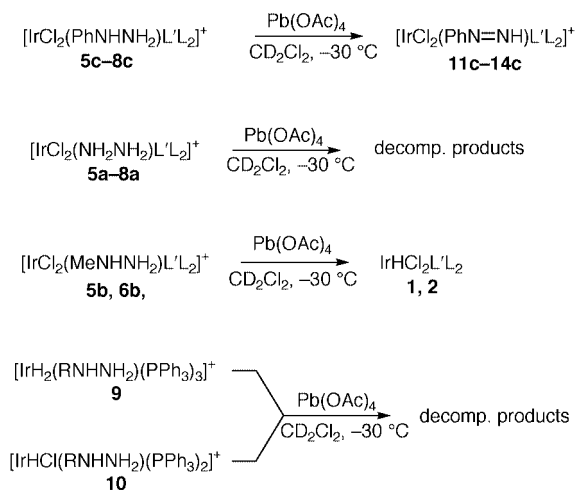
Scheme 4 $L' = PPh(OEt)_2$ or $P(OEt)_3$; $L = PPh_3$ or $AsPh_3$; $R = H$ or Me.

$IrHCl_2[P(OEt)_3](PPh_3)_2$ 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
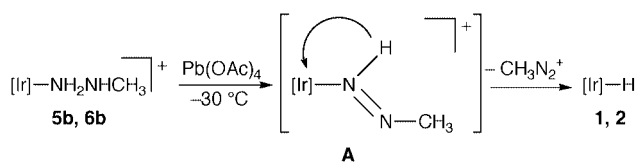

Scheme 5 $[Ir] = IrCl_2PL_2$.

$\{[Ir]\text{–NH=NMe}\}^+$ **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.

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 $IrHCl_2L'L_2$ **1–4** with aryldiazonium cations, in order to test an alternative synthesis of $\{[Ir]\text{–ArN=}NH\}^+$ derivatives. The results are summarised in Scheme 6.

Both mono- ArN_2^+ and bis- $[N_2Ar\text{–}ArN_2]^{2+}$ aryldiazonium cations react with hydrides **1–4** to give aryldiazene complexes $[IrCl_2(ArN=NH)L'L_2]^+$ **11–14** and $[\{IrCl_2L'L_2\}_2(\mu\text{-}NH=NAr\text{–}ArN=NH)]^{2+}$ **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 $(-80\,°C)$
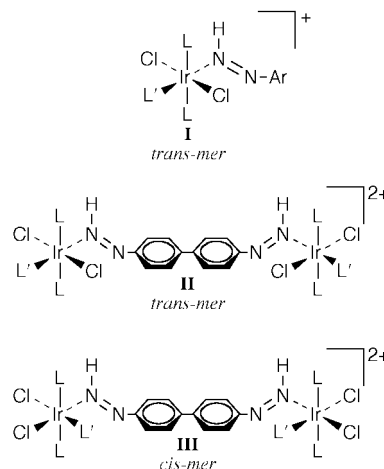
Fig. 4 $L = PPh_3$ or $AsPh_3$, $L' = PPh(OEt)_2$ or $P(OEt)_3$.
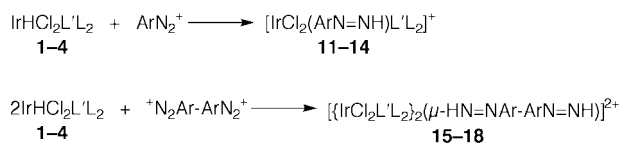
Scheme 6 $L = PPh_3$, $L' = PPh(OEt)_2$ **11**, **15** (**c**,**f**); $L = PPh_3$, $L' = P(OEt)_3$ **12** (**c–f**), **16c**; $L = AsPh_3$, $L' = PPh(OEt)_2$ **13c**, **17c**; $L = AsPh_3$, $L' = P(OEt)_3$ **14** (**c–f**), **18c**; $Ar = Ph$ **c** or $C_6H_4Me\text{-}4$ **f**; $Ar\text{–}Ar = 4,4'\text{-}C_6H_4\text{–}C_6H_4$ **c** or $4,4'\text{-}(2\text{-}Me)C_6H_3\text{–}C_6H_3(Me\text{-}2)$ **f**.

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.

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 ^1H 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 $^1J_{^{15}NH}$ and $^2J_{^{15}NH}$, 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 $^{31}P\{^1H\}$ NMR spectra show only one AB_2 multiplet for the PPh_3 derivatives and a sharp singlet for the $AsPh_3$ ones, whereas the ^1H 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 $\nu(IrCl)$ 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 $\nu(IrCl)$ 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$_2$L′L$_2$. This reaction also allows the binuclear complexes [{IrCl$_2$L′L$_2$}$_2$(μ-HN=NAr–ArN=NH)]-(BPh$_4$)$_2$ containing the bis(aryldiazene) bridging ligand to be prepared.

Acknowledgements

References

1 H. Zollinger, *Diazo Chemistry II*, VCH, Weinheim, 1995; D. Sutton, *Chem. Rev.*, 1993, **93**, 995; H. Kisch and P. Holzmeier, *Adv. Organomet. Chem.*, 1992, **34**, 67; B. F. G. Johnson, B. L. Haymore and J. R. Dilworth, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2; R. A. Henderson, G. J. Leigh and C. J. Pickett, *Adv. Inorg. Chem. Radiochem.*, 1983, **27**, 197; F. Bottomley, *Q. Rev. Chem. Soc.*, 1970, **24**, 617.

2 M. Hidai and Y. Mizobe, *Chem. Rev.*, 1995, **95**, 1115; R. R. Eady and G. J. Leigh, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 2739; D. Sellmann, *Angew. Chem.*, *Int. Ed. Engl.*, 1993, **32**, 64.

3 K. D. Demadis, S. M. Malinak and D. Coucouvanis, *Inorg. Chem.*, 1996, **35**, 4038; C. J. Davies, I. M. Dodd, M. M. Harding, B. T. Heaton, C. Jacob and J. Ratnam, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 787; T.-Y. Cheng, A. Ponce, A. L. Rheingold and G. L. Hillhouse, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 657; D. Sellmann, J. Käppler, M. Moll and F. Knoch, *Inorg. Chem.*, 1993, **32**, 960; T. E. Glassman, M. G. Vale and R. R. Schrock, *J. Am. Chem. Soc.*, 1992, **114**, 8098; M. Kawano, C. Hoshino and K. Matsumoto, *Inorg. Chem.*, 1992, **31**, 5158.

4 B. K. Burgess, S. Wherland, E. I. Stiefel and W. E. Newton, *Biochemistry*, 1981, **20**, 5140; L. C. Davis, *Arch. Biochem. Biophys.*, 1980, 204.

5 M. J. Dilworth and R. R. Eady, *Biochem. J.*, 1991, **277**, 465; R. N. Thorneley and D. J. Lowe, *Biochem. J.*, 1984, **224**, 887; D. J. Evans, R. A. Henderson and B. E. Smith, in *Bioinorganic Catalysis*, ed. J. Reedijk, Marcel Dekker Inc., New York, 1993; R. N. Thorneley, R. R. Eady and D. J. Lowe, *Nature (London)*, 1978, **272**, 557.

6 X. Yan, R. J. Batchelor, F. W. B. Einstein, X. Zhang, R. Nagelkerke and D. Sutton, *Inorg. Chem.*, 1997, **36**, 1237 and references therein; M. Cowie, I. R. McKeer, S. J. Loeb and M. D. Gauthier, *Organometallics*, 1986, **5**, 860; M. Angoletta and G. Caglio, *J. Organomet. Chem.*, 1982, **234**, 99; K. D. Schramm and J. A. Ibers, *Inorg. Chem.*, 1980, **19**, 2435; A. B. Gilchrist and D. Sutton, *J. Chem. Soc.*, *Dalton Trans.*, 1977, 677; J. A. Carroll, R. E. Cobbledick, F. W. B. Einstein, N. Farrell, D. Sutton and P. L. Vogel, *Inorg. Chem.*, 1977, **16**, 2462; M. Cowie, B. L. Haymore and J. A. Ibers, *J. Am. Chem. Soc.*, 1976, **98**, 7608; F. W. B. Einstein and D. Sutton, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 434; F. W. B. Einstein, A. B. Gilchrist, G. W. Rayner-Canham and D. Sutton, *J. Am. Chem. Soc.*, 1972, **94**, 645; A. J. Deeming and B. L. Shaw, *J. Chem. Soc. A*, 1969, 1128.

7 G. Albertin, S. Antoniutti and E. Bordignon, *J. Chem. Soc.*, *Chem. Commun.*, 1984, 1688; G. Albertin, S. Antoniutti, G. Pelizzi, F. Vitali and E. Bordignon, *J. Am. Chem. Soc.*, 1986, **108**, 6627; G. Albertin and E. Bordignon, *J. Chem. Soc.*, *Dalton Trans.*, 1986, 2551; G. Albertin, S. Antoniutti and E. Bordignon, *Inorg. Chem.*, 1987, **26**, 3416; G. Albertin, S. Antoniutti and E. Bordignon, *J. Am. Chem. Soc.*, 1989, **111**, 2072; G. Albertin, S. Antoniutti and E. Bordignon, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 2553; G. Albertin, P. Amendola, S. Antoniutti and E. Bordignon, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 2979; G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, G. Pelizzi and P. Ugo, *Inorg. Chem.*, 1996, **35**, 6245.

8 G. Albertin, S. Antoniutti, E. Bordignon and S. Pattaro, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 4445; G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, P. M. Dolcetti and G. Pelizzi, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 4435; G. Albertin, S. Antoniutti, A. Bacchi, M. Bergamo, E. Bordignon and G. Pelizzi, *Inorg. Chem.*, 1998, **37**, 479.

9 R. Rabinowitz and J. Pellon, *J. Org. Chem.*, 1961, **26**, 4623.

10 E. Nachbaur and G. Leiseder, *Monatsh. Chem.*, 1971, **102**, 1718.

11 A. I. Vogel, in *Practical Organic Chemistry*, 3rd edn., Longmans, Green and Co., New York, 1956.

12 G. Balacco, *J. Chem. Inf. Comput. Sci.*, 1994, **34**, 1235.

13 (*a*) S. Park, A. J. Lough and R. H. Morris, *Inorg. Chem.*, 1996, **35**, 3001 and references therein; (*b*) R. C. Taylor, J. F. Young and G. Wilkinson, *Inorg. Chem.*, 1966, **5**, 20; (*c*) N. Ahmad, S. D. Robinson and M. F. Uttley, *J. Chem. Soc.*, *Dalton Trans.*, 1972, 843.

14 J. R. Ferraro, *Low-Frequency Vibrations of Inorganic and Coordination Compounds*, Plenum Press, New York, 1971.

15 R. H. Crabtree, M. Lavin and L. Bonneviot, *J. Am. Chem. Soc.*, 1986, **108**, 4032.

16 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

17 M. R. Smith, III, R. L. Keys, G. L. Hillhouse and A. L. Rheingold, *J. Am. Chem. Soc.*, 1989, **111**, 8312; M. N. Ackermann, *Inorg. Chem.*, 1971, **10**, 272.

18 M. R. Smith, III, T.-Y. Cheng and G. L. Hillhouse, *J. Am. Chem. Soc.*, 1993, **115**, 8638; D. Sellmann, W. Soglowek, F. Knoch and M. Moll, *Angew. Chem.*, *Int. Ed. Engl.*, 1989, **28**, 1271.

19 T.-Y. Cheng, J. C. Peters and G. L. Hillhouse, *J. Am. Chem. Soc.*, 1994, **116**, 204.

20 K. R. Laing, S. D. Robinson and M. F. Uttley, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 2713; J. A. Carroll, D. Sutton and Z. Xiaoheng, *J. Organomet. Chem.*, 1982, **244**, 73.

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