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Synthesis, characterisation and reactivity of hydrazine complexes of iron(II)

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Hydrazine complexes $[Fe(R^1NHNH_2)(R^2CN)L_4][BPh_4]_2$ **1**–**3** and $[FeH(R^1NHNH_2)L_4]BPh_4$ **4** [R^1 = H, Me, Ph, $4-MeC_6H_4$, $4-ClC_6H_4$, $4-O_2NC_6H_4$ or Me_2NNH_2; R^2 = $4-MeC_6H_4$, Me or Ph; L = $P(OEt)_3$, $P(OMe)_3$ or $PPh(OEt)_2$] were prepared by reacting nitrile complexes $[Fe(R^2CN)_2L_4][BPh_4]_2$ and $[FeH(R^2CN)L_4]BPh_4$ with an excess of the appropriate hydrazine. Their formulation and geometry in solution were established by infrared and ^1H and ^{31}P NMR spectroscopy. Amidrazone derivatives $[Fe\{\eta^2-NH{=}C(R^2)NR^1NH_2\}L_4][BPh_4]_2$ [R^2 = $4-MeC_6H_4$, Me or Ph; R^1 = H or Me; L = $P(OEt)_3$ or $P(OMe)_3$] were obtained by allowing nitrilehydrazine complexes to react in solution and their formation, involving a nucleophilic attack of the hydrazine on the cyanide carbon atom of the R^2CN ligand, is also discussed. Reaction of the arylhydrazine complexes **1**–**4** with $Pb(O_2CMe)_4$ at −30 °C in CH_2Cl_2 resulted in selective oxidation of the arylhydrazine ligand affording the aryldiazene $[Fe(R^1N{=}NH)(R^2CN)L_4][BPh_4]_2$ and $[FeH(R^1N{=}NH)L_4]BPh_4$ **10** [R^1 = aryl; L = $P(OEt)_3$ or $P(OMe)_3$] derivatives. Treatment of the arylhydrazine $[Fe(R^1NHNH_2)(R^2CN)\{P(OEt)_3\}_4][BPh_4]_2$ **1** (R^1 = Ph or $4-MeC_6H_4$) with an excess of NEt_3 resulted in a complicated reaction giving the five-co-ordinate aryldiazenido derivatives $[Fe(R^1N_2)\{P(OEt)_3\}_4]BPh_4$.

Among the transition-metal complexes containing partially reduced dinitrogen ligands[1,2] the hydrazine derivatives are about the least studied and, although several papers have recently appeared,[3] many aspects of the chemistry of co-ordinated hydrazine still remain unclear. The interest in this class of compounds is due in part to their relevance to the nitrogen fixation process, in which co-ordinated hydrazine is considered as a possible intermediate.[1,2] Hydrazine is, in fact, a substrate[4] as well as a product of functioning nitrogenase and has been isolated by quenching the enzyme.[5] Furthermore, the co-ordination chemistry of hydrazine and substituted hydrazines presents some aspects of interest, including the influence that the ancillary ligands and the central metal may have in determining the different co-ordination modes, *i.e.* η^1, η^2, μ, *etc.* of the hydrazine ligand and the understanding of the properties that co-ordination to a metal fragment may induce on an NH_2NH_2 or $RNHNH_2$ molecule towards reduction, oxidation and deprotonation reactions.

We have previously reported[6] on the synthesis and the reactivity of aryldiazenido $M(N_2R)$ and aryldiazene $M(HN{=}NR)$ derivatives of the iron family and now we have extended these studies[7] to include hydrazine and some substituted hydrazines as ligands and in this paper we report the synthesis and some novel reactions of hydrazine derivatives of iron(II).

Relatively few complexes of iron containing hydrazine ligands have been described[8–10] and, apart from the polymeric[9] $[FeX_2(RNHNH_2)_2]$ and $[Fe(RNHNH_2)_3][NO_3]_2$ (X = F, Cl, Br or I; R = H, Me, $4-O_2NC_6H_4$ or $4-ClC_6H_4$) derivatives, nearly all contain the polydentate NS_4-, OS_4- or S_5-type ligands.[8] With phosphine or carbonyl as ancillary groups, the hydrazine complexes are rare,[10] including only $[Fe(cp)(CO)_2(N_2H_4)]X$ {cp = $\eta^5-C_5H_5$, X = BPh_4^- or $[Cr(NH_3)_2(SCN)_4]^-$},[10a] $[Fe(cp)(NH_2NH_2)(dppe)]PF_6$ (dppe = $Ph_2PCH_2CH_2PPh_2$)[10b] and $[Fe(RNHNH_2)(CO)\{P(OEt)_3\}_4]BPh_4$ (R = $4-MeC_6H_4$, $4-MeOC_6H_4$ or $4-O_2NC_6H_4$),[10c] and therefore it should be of interest to report the synthesis of new hydrazine iron(II) complexes along with some new properties shown by this class of compounds.

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 relatively stable in air, but were stored under an inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line and distilled into vacuum-tight storage flasks. The phosphites $P(OMe)_3$ and $P(OEt)_3$ (Aldrich) were purified by distillation under nitrogen, while $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon.[11] The hydrazines $MeNHNH_2$, $PhNHNH_2$, $4-O_2NC_6H_4NHNH_2$, $PhCONHNH_2$ and Me_2NNH_2 were Aldrich products used as received. The compounds $4-MeC_6H_4NHNH_2$ and $4-ClC_6H_4NHNH_2$ were prepared by treating under nitrogen the corresponding salts $RNHNH_3^+Cl^-$ with a slight excess of NaOH in aqueous solution. A solid separated which, after 15 min of stirring, was filtered off, washed with water and dried over P_2O_5 under vacuum for 24 h. The solid was stored under nitrogen at −25 °C. Hydrazine NH_2NH_2 was prepared by decomposition of hydrazine cyanurate (Fluka) following the reported method.[12] Triethylamine was dried with CaH_2 and distilled before use. Other reagents were from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer, NMR spectra (^1H, ^{31}P) on a Bruker AC200 spectrometer at temperatures varying between −90 and +30 °C, unless otherwise noted. The SWANMR software package[13] has been used in treating the NMR data. Proton NMR spectra were referenced to internal tetramethylsilane, $^{31}P-\{^1H\}$ chemical shifts with respect to 85% H_3PO_4, with downfield shifts considered positive. The conductivities of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83 instrument.

Synthesis of complexes

The nitrile complexes $[FeH(R^2CN)L_4]BPh_4$ (R^2 = $4-MeC_6H_4$ or Me) were prepared following the method previously reported.[6f]

$[Fe(R^2CN)_2L_4][BPh_4]_2$ [L = $P(OEt)_3$, $P(OMe)_3$ or $PPh(OEt)_2$; R^2 = $4-MeC_6H_4$, Me or Ph]. An excess of the appropriate phosphite (42 mmol) was added to a solution of anhydrous $FeCl_2$ (10 mmol, 1.27 g) in ethanol (20 cm^3) (or methanol) and the reaction mixture was refluxed for 90 min. After cooling to room temperature, the appropriate nitrile (20 mmol) was slowly added and the resulting solution stirred for 30–40 min. The addition of a slight excess of NaBPh$_4$ (22 mmol, 7.53 g) in ethanol (10 cm^3) (or methanol) caused the precipitation of a yellow solid which was filtered off and crystallised from CH$_2$Cl$_2$ (10 cm^3) and alcohol (30 cm^3); yield ⩾75% [L = P(OEt)$_3$, R^2 = 4-MeC$_6$H$_4$: Found C, 66.3; H, 7.2; N, 1.7. $C_{88}H_{114}B_2FeN_2O_{12}P_4$ requires C, 66.3; H, 7.2; N, 1.8%; m.p. 122 °C; Λ_M = 125.2 S cm^2 mol^{-1}. L = P(OEt)$_3$, R^2 = Me: Found C, 63.2; H, 7.2; N, 1.9. $C_{76}H_{106}B_2FeN_2O_{12}P_4$ requires C, 63.35; H, 7.4; N, 1.9%; m.p. 115 °C; Λ_M = 135.2 S cm^2 mol^{-1}. L = P(OEt)$_3$, R^2 = Ph: Found C, 66.15; H, 7.2; N, 1.8. $C_{86}H_{110}B_2FeN_2O_{12}P_4$ requires C, 66.0; H, 7.1; N, 1.8%; m.p. 117 °C; Λ_M = 122.4 S cm^2 mol^{-1}. L = P(OMe)$_3$, R^2 = Me: Found C, 60.4; H, 6.5; N, 2.1. $C_{64}H_{82}B_2FeN_2O_{12}P_4$ requires C, 60.4; H, 6.5; N, 2.2; m.p. 165 °C; Λ_M = 124.8 S cm^2 mol^{-1}. L = PPh(OEt)$_2$, R^2 = 4-MeC$_6$H$_4$: Found C, 72.5; H, 6.6; N, 1.6. $C_{104}H_{114}B_2FeN_2O_8P_4$ requires C, 72.6; H, 6.7; N, 1.6%; m.p. 121 °C; Λ_M = 118.7 S cm^2 mol^{-1}. L = PPh(OEt)$_2$, R^2 = Me: Found C, 70.2; H, 6.7; N, 1.8. $C_{92}H_{106}B_2FeN_2O_8P_4$ requires C, 70.4; H, 6.8; N, 1.8%; m.p. 133 °C; Λ_M = 121.4 S cm^2 mol^{-1}].

[Fe(R^{1}NHNH$_2$)(4-MeC$_6$H$_4$CN)L$_4$][BPh$_4$]$_2$ [L = P(OEt)$_3$ 1t or PPh(OEt)$_2$ 3t; R^1 = H a, Me b, Ph c, 4-MeC$_6$H$_4$ d, 4-ClC$_6$H$_4$ e or 4-O$_2$NC$_6$H$_4$ f]. An excess of the appropriate hydrazine (14 mmol) was added at room temperature to a solution of the bis(nitrile) complex [Fe(R^{2}CN)$_2$L$_4$][BPh$_4$]$_2$ (2 mmol) in dichloromethane (30 cm^3) and the reaction mixture was stirred for 5–7 h in the case of NH$_2$NH$_2$ and for 24 h with the other hydrazines. The resulting solution was filtered and then evaporated to dryness to give a brown oil which was treated with ethanol (10 cm^3). The addition of an excess of NaBPh$_4$ (3 mmol, 1.0 g) in ethanol (5 cm^3) to the resulting solution caused the precipitation of a yellow solid which was filtered off and crystallised from CH$_2$Cl$_2$ (5 cm^3) and ethanol (15 cm^3); yield between 30 and 50% (Found: C, 63.8; H, 7.3; N, 2.7. $C_{80}H_{111}B_2FeN_3O_{12}P_4$ **1ta** requires C, 63.7; H, 7.4; N, 2.8%; m.p. 123 °C; Λ_M = 123.9 S cm^2 mol^{-1}. Found: C, 65.05; H, 7.3; N, 2.5. $C_{86}H_{115}B_2FeN_3O_{12}P_4$ **1tc** requires C, 65.2; H, 7.3; N, 2.65%; m.p. 120 °C; Λ_M = 127.6 S cm^2 mol^{-1}. Found: C, 65.3; H, 7.2; N, 2.7. $C_{87}H_{117}B_2FeN_3O_{12}P_4$ **1td** requires C, 65.4; H, 7.4; N, 2.6%; m.p. 123 °C; Λ_M = 123.9 S cm^2 mol^{-1}. Found: C, 63.6; H, 7.15; N, 2.5. $C_{86}H_{114}B_2ClFeN_3O_{12}P_4$ **1te** requires C, 63.8; H, 7.1; N, 2.6%; m.p. 114 °C; Λ_M = 124.5 S cm^2 mol^{-1}. Found: C, 70.3; H, 6.75; N, 2.5. $C_{96}H_{111}B_2FeN_3O_8P_4$ **3ta** requires C, 70.5; H, 6.8; N, 2.6%; m.p. 111 °C; Λ_M = 125.6 S cm^2 mol^{-1}. Found: C, 70.5; H, 6.8; N, 2.45. $C_{97}H_{113}B_2FeN_3O_8P_4$ **3tb** requires C, 70.6; H, 6.9; N, 2.55%; m.p. 109 °C; Λ_M = 129.1 S cm^2 mol^{-1}. Found: C, 71.4; H, 6.7; N, 2.4. $C_{102}H_{115}B_2FeN_3O_8P_4$ **3tc** requires C, 71.5; H, 6.8; N, 2.45%; m.p. 121 °C; Λ_M = 119.9 S cm^2 mol^{-1}. Found: C, 71.7; H, 6.75; N, 2.4. $C_{103}H_{117}B_2FeN_3O_8P_4$ **3td** requires C, 71.7; H, 6.8; N, 2.4%; m.p. 118 °C; Λ_M = 125.0 S cm^2 mol^{-1}).

[Fe(Me$_2$NNH$_2$)(4-MeC$_6$H$_4$CN){P(OEt)$_3$}$_4$][BPh$_4$]$_2$ 1tg. This complex was prepared exactly like the related compounds **1** treating [Fe(4-MeC$_6$H$_4$CN)$_2${P(OEt)$_3$}$_4$][BPh$_4$]$_2$ with an excess of Me$_2$NNH$_2$ in CH$_2$Cl$_2$ for 24 h; yield ⩾35% (Found: C, 64.3; H, 7.5; N, 2.7. $C_{82}H_{115}B_2FeN_3O_{12}P_4$ requires C, 64.1; H, 7.55; N, 2.7%), m.p. 103 °C, Λ_M = 121.8 S cm^2 mol^{-1}.

[Fe(R^{1}NHNH$_2$)(MeCN)L$_4$][BPh$_4$]$_2$ [L = P(OEt)$_3$ 1a, P(OMe)$_3$ 2a or PPh(OEt)$_2$ 3a; R^1 = H a, Me b, Ph c, 4-MeC$_6$H$_4$ d, 4-ClC$_6$H$_4$ e and 4-O$_2$NC$_6$H$_4$ f]. These complexes were prepared exactly like the related *p*-toluonitrile compounds **1t** and **3t** treating [Fe(MeCN)$_2$L$_4$][BPh$_4$]$_2$ with an excess of the appropriate hydrazine; yield between 30 and 50% (Found: C, 62.2; H, 7.45; N, 2.8. $C_{74}H_{107}B_2FeN_3O_{12}P_4$ **1aa** requires C, 62.1; H, 7.5; N, 2.9%; m.p. 122 °C; Λ_M = 127.4 S cm^2 mol^{-1}. Found: C, 63.5; H, 7.4; N, 2.7. $C_{80}H_{111}B_2FeN_3O_{12}P_4$ **1ac** requires C, 63.7; H, 7.4; N, 2.8%; m.p. 120 °C; Λ_M = 121.2 S cm^2 mol^{-1}. Found: C, 63.7; H, 7.4; N, 2.8. $C_{81}H_{113}B_2FeN_3O_{12}P_4$ **1ad** requires C, 63.9; H, 7.5; N, 2.8%; m.p. 124 °C; Λ_M = 126.4 S cm^2 mol^{-1}. Found: C, 61.6; H, 7.1; N, 3.7. $C_{80}H_{110}B_2FeN_4O_{14}P_4$ **1af** requires C, 61.9; H, 7.1; N, 3.6%; m.p. 101 °C; Λ_M = 126.7 S cm^2 mol^{-1}. Found: C, 58.8; H, 6.5; N, 3.25. $C_{62}H_{83}B_2FeN_3O_{12}P_4$ **2aa** requires C, 58.9; H, 6.6; N, 3.3%; m.p. 170 °C; Λ_M = 122.9 S cm^2 mol^{-1}. Found: C, 61.1; H, 6.6; N, 3.05. $C_{68}H_{87}B_2FeN_3O_{12}P_4$ **2ac** requires C, 61.0; H, 6.55; N, 3.1%; m.p. 175 °C; Λ_M = 118.9 S cm^2 mol^{-1}. Found: C, 70.6; H, 6.7; N, 2.6. $C_{96}H_{111}B_2FeN_3O_8P_4$ **3ac** requires C, 70.5; H, 6.8; N, 2.6%; m.p. 129 °C; Λ_M = 120.8 S cm^2 mol^{-1}. Found: C, 70.4; H, 6.8; N, 2.4. $C_{97}H_{113}B_2FeN_3O_8P_4$ **3ad** requires C, 70.6; H, 6.9; N, 2.55%; m.p. 126 °C; Λ_M = 126.7 S cm^2 mol^{-1}).

[Fe(NH$_2$NH$_2$)(PhCN){P(OEt)$_3$}$_4$][BPh$_4$]$_2$ 1ba. This complex was prepared exactly like the related compounds **1ta** and **1aa** treating [Fe(PhCN)$_2${P(OEt)$_3$}$_4$][BPh$_4$]$_2$ with an excess of NH$_2$NH$_2$ in CH$_2$Cl$_2$ for about 7 h; yield ⩾35% (Found: C, 63.6; H, 7.5; N, 2.7. $C_{79}H_{109}B_2FeN_3O_{12}P_4$ requires C, 63.5; H, 7.35; N, 2.8%), m.p. 114 °C, Λ_M = 128.1 S cm^2 mol^{-1}.

[FeH(R^{1}NHNH$_2$){P(OEt)$_3$}$_4$]BPh$_4$ 4 (R^1 = H a, Ph c, 4-MeC$_6$H$_4$ d or 4-O$_2$NC$_6$H$_4$ f). To a solution of [FeH(4-MeC$_6$H$_4$CN){P(OEt)$_3$}$_4$]BPh$_4$ (1 mmol, 1.2 g) in dichloromethane (20 cm^3) was added an excess of the appropriate hydrazine and the reaction mixture was stirred at room temperature for 8 h. The solvent was removed under reduced pressure to give an oil which was treated with ethanol containing an excess of NaBPh$_4$ (2 mmol, 0.68 g). A yellow solid slowly separated which was filtered off and crystallised from ethanol; yield ⩾65% (Found: C, 54.4; H, 8.0; N, 2.5. $C_{48}H_{85}BFeN_2O_{12}P_4$ **4a** requires C, 53.7; H, 8.0; N, 2.6%; m.p. 98 °C; Λ_M = 60.1 S cm^2 mol^{-1}. Found: C, 56.2; H, 7.8; N, 2.5. $C_{54}H_{89}BFeN_2O_{12}P_4$ **4c** requires C, 56.5; H, 7.8; N, 2.4%; Λ_M = 61.1 S cm^2 mol^{-1}. Found: C, 56.7; H, 7.8; N, 2.45. $C_{55}H_{91}BFeN_2O_{12}P_4$ **4d** requires C, 56.8; H, 7.9; N, 2.4%; m.p. 88 °C; Λ_M = 59.3 S cm^2 mol^{-1}. Found: C, 54.5; H, 7.35; N, 3.6. $C_{54}H_{88}BFeN_3O_{14}P_4$ **4f** requires C, 54.3; H, 7.4; N, 3.5%; m.p. 90 °C; Λ_M = 58.7 S cm^2 mol^{-1}).

[Fe(η^2-PhCONHNH$_2$){P(OEt)$_3$}$_4$][BPh$_4$]$_2$ 5. An excess of solid benzoylhydrazine (20 mmol, 2.7 g) was added to a solution of [Fe(4-MeC$_6$H$_4$CN)$_2${P(OEt)$_3$}$_4$][BPh$_4$]$_2$ (2 mmol, 3.2 g) in CH$_2$Cl$_2$ (50 cm^3) and the resulting suspension stirred for 48 h. The reaction mixture was filtered and the solvent removed under reduced pressure to give a green oil which was treated with ethanol (15 cm^3) containing an excess of NaBPh$_4$ (3 mmol, 1.0 g). A yellow solid slowly separated from the stirred solution which was filtered off and rejected. The solution was then cooled to −25 °C and stirred until a solid separated which was filtered off and crystallised from ethanol; yield ⩾40% (Found: C, 63.4; H, 7.4; N, 1.9. $C_{79}H_{108}B_2FeN_2O_{13}P_4$ requires C, 63.5; H, 7.3; N, 1.9%), m.p. 128 °C, Λ_M = 122.2 S cm^2 mol^{-1}.

[Fe{η^2-NH=C(R^2)NHNH$_2$}{P(OEt)$_3$}$_4$][BPh$_4$]$_2$ (R^2 = MeC$_6$H$_4$ 6ta or Me 6aa). Hydrazine complexes [Fe(NH$_2$NH$_2$)(R^{2}CN){P(OEt)$_3$}$_4$][BPh$_4$]$_2$ **1ta** and **1aa** (1 mmol) were dissolved in acetone (10 cm^3) and the solution stirred for 2 h. The solvent was removed under reduced pressure giving an oil which was treated with ethanol (5 cm^3). The resulting solution was stirred until a solid separated which was filtered off, washed with ethanol and dried under vacuum; yield ⩾90% (Found: C, 63.9; H, 7.4; N, 2.6. $C_{80}H_{111}B_2FeN_3O_{12}P_4$ **6ta** requires C, 63.7; H, 7.4; N, 2.8%; m.p. 135 °C; Λ_M = 128.9 S cm^2 mol^{-1}. Found: C, 62.2; H, 7.6; N, 2.95. $C_{74}H_{107}B_2FeN_3O_{12}P_4$ **6aa** requires C, 62.1; H, 7.5; N, 2.9%; m.p. 138 °C; Λ_M = 126.8 S cm^2 mol^{-1}).

[Fe{η^2-NH=C(Ph)NHNH$_2$}{P(OEt)$_3$}$_4$][BPh$_4$]$_2$ 6ba. This complex was prepared exactly like the related **6ta** and **6aa** starting from **1ba**; yield ⩾95% (Found: C, 63.6; H, 7.45; N, 2.7. $C_{79}H_{109}B_2FeN_3O_{12}P_4$ requires C, 63.5; H, 7.35; N, 2.8%), m.p. 135 °C, Λ_M = 127.2 S cm^2 mol^{-1}.

$[Fe\{\eta^2\text{-}NH{=}C(R^2)N(Me)NH_2\}\{P(OEt)_3\}_4][BPh_4]_2$ 6tb–6ab and $[Fe\{\eta^2\text{-}NH{=}C(R^2)N(Me)NH_2\}\{P(OMe)_3\}_4][BPh_4]_2$ 7ab (R^2 = 4-MeC_6H_4 t or Me a). These complexes were obtained in an attempt to prepare the methylhydrazine complexes $[Fe(MeNHNH_2)(R^2CN)L_4][BPh_4]_2$ following the method reported for **1**–**3**. A typical preparation involved the treatment of $[Fe(R^2CN)_2L_4][BPh_4]_2$ (2 mmol) dissolved in CH_2Cl_2 (30 cm^3) with an excess of methylhydrazine (20 mmol, 1.1 cm^3) for about 5 h. After removal of the solvent under reduced pressure, the remaining oil was treated with ethanol or methanol (10 cm^3) containing an excess of $NaBPh_4$ (3 mmol, 1.0 g). A yellow solid slowly separated which was filtered off and crystallised from CH_2Cl_2 (5 cm^3) and the appropriate alcohol (15 cm^3); yield ⩾80% (Found: C, 64.1; H, 7.5; N, 2.8. $C_{81}H_{113}B_2FeN_3O_{12}P_4$ **6tb** requires C, 63.9; H, 7.5; N, 2.8%; m.p. 136 °C; Λ_M = 129.5 S cm^2 mol^{-1}. Found: C, 62.4; H, 7.5; N, 2.8. $C_{75}H_{109}B_2FeN_3O_{12}P_4$ **6ab** requires C, 62.3; H, 7.6; N, 2.9%; m.p. 148 °C; Λ_M = 131.6 S cm^2 mol^{-1}. Found: C, 59.0; H, 6.5; N, 3.2. $C_{63}H_{85}B_2FeN_3O_{12}P_4$ **7ab** requires C, 59.2; H, 6.7; N, 3.3%; Λ_M = 128.1 S cm^2 mol^{-1}).

$[Fe(R^1N{=}NH)(4\text{-}MeC_6H_4CN)\{P(OEt)_3\}_4][BPh_4]_2$ 8t (R^1 = Ph c or 4-MeC_6H_4 d). A sample of $[Fe(R^1NHNH_2)(R^2CN)L_4][BPh_4]_2$ (0.5 mmol) was placed in a three-necked flask (25 cm^3) fitted with a solid-addition sidearm containing an excess of $Pb(O_2CMe)_4$ (1.5 mmol, 0.66 g). Dichloromethane (20 cm^3) was added, the solution cooled to −30 °C and the $Pb(O_2CMe)_4$ added portionwise over 30–40 min to the cold stirred solution. The solution was then filtered and the solvent removed under reduced pressure to give an oil. The addition of ethanol (5 cm^3) containing an excess of $NaBPh_4$ (1.5 mmol, 0.51 g) caused the separation of an orange solid which was filtered off and crystallised from CH_2Cl_2 (3 cm^3) and ethanol (10 cm^3); yield ⩾70% (Found: C, 65.05; H, 7.2; N, 2.8. Calc. for $C_{86}H_{113}B_2FeN_3O_{12}P_4$ **8tc**: C, 65.3; H, 7.2; N, 2.7%; Λ_M = 122.4 S cm^2 mol^{-1}. Found: C, 65.3; H, 7.4; N, 2.5. Calc. for $C_{87}H_{115}B_2FeN_3O_{12}P_4$ **8td**: C, 65.5; H, 7.3; N, 7.3%; Λ_M = 126.7 S cm^2 mol^{-1}).

$[Fe(PhN{=}NH)(MeCN)\{P(OMe)_3\}_4][BPh_4]_2$ 9ac. This complex was prepared exactly like **8ac** by oxidation with $Pb(O_2CMe)_4$ of $[Fe(PhNHNH_2)(MeCN)\{P(OMe)_3\}_4][BPh_4]_2$, but was obtained as an oily product. The ^1H NMR spectrum, however, confirmed the presence of the aryldiazene ligand.

$[FeH(4\text{-}MeC_6H_4N{=}NH)\{P(OEt)_3\}_4]BPh_4$ 10d. This complex was prepared by oxidation with an excess of $Pb(O_2CMe)_4$ of the hydrazine complex $[FeH(4\text{-}MeC_6H_4NHNH_2)\{P(OEt)_3\}_4]BPh_4$ at −30 °C in CH_2Cl_2; yield ⩾80% (Found: C, 56.8; H, 7.6; N, 2.3. Calc. for $C_{55}H_{93}BFeN_2O_{12}P_4$: C, 56.9; H, 7.7; N, 2.4%), Λ_M = 49.2 S cm^2 mol^{-1}.

$[Fe(R^1N_2)\{P(OEt)_3\}_4]BPh_4$ 11 (R^1 = Ph c or 4-MeC_6H_4 d). An excess of triethylamine (5 mmol, 0.7 cm^3) was added to a solution of $[Fe(R^1NHNH_2)(R^2CN)\{P(OEt)_3\}_4][BPh_4]_2$ (1 mmol) in CH_2Cl_2 (10 cm^3) and the reaction mixture stirred for 24 h. A white solid of $[NHEt_3]BPh_4$ began to separate after 1–2 h which was, at the end, filtered off. The solution was evaporated to dryness under reduced pressure giving a red-brown oil which was treated with ethanol (5 cm^3) containing an excess of $NaBPh_4$ (2 mmol, 0.68 g). A solid slowly separated from the resulting solution which was filtered off. By slow cooling to −25 °C red crystals of the complex slowly separated from the solution which were filtered off and dried under vacuum; yield between 10 and 20% (Found: C, 56.5; H, 7.55; N, 2.3. Calc. for $C_{54}H_{85}BFeN_2O_{12}P_4$ **11c**: C, 56.65; H, 7.5; N, 2.45%. Found: C, 56.8; H, 7.7; N, 2.3. Calc. for $C_{55}H_{87}BFeN_2O_{12}P_4$ **11d** C, 57.0; H, 7.6; N, 2.4%; Λ_M = 53.7 S cm^2 mol^{-1}).

Table 1 Hydrazine complexes prepared: NH_2NH_2 **a**, $MeNHNH_2$ **b**, $PhNHNH_2$ **c**, 4-$MeC_6H_4NHNH_2$ **d**, 4-$ClC_6H_4NHNH_2$ **e**, 4-$O_2NC_6H_4NHNH_2$, **f**, Me_2NNH_2 **g**

	R^2		
L	4-MeC_6H_4	Me	Ph
$P(OEt)_3$	**1t**	**1a**	**1b**
$P(OMe)_3$		**2a**	
$PPh(OEt)_2$	**3t**	**3a**	

$$[Fe(R^2CN)_2L_4][BPh_4]_2 \xrightarrow{\text{excess of } R^1NHNH_2} [Fe(R^1NHNH_2)(R^2CN)L_4][BPh_4]_2$$

1t, **3t**, **1a**–**3a**, **1b**

$$[FeH(R^2CN)\{P(OEt)_3\}_4]BPh_4 \xrightarrow{\text{excess of } R^1NHNH_2} [FeH(R^1NHNH_2)\{P(OEt)_3\}_4]BPh_4$$

4

Scheme 1 L = $P(OEt)_3$ **1**, $P(OMe)_3$ **2**, $PPh(OEt)_2$ **3**; R^1 = H **a**, Me **b**, Ph **c**, 4-MeC_6H_4 **d**, 4-ClC_6H_4 **e**, 4-$O_2NC_6H_4$ **f**, Me_2NNH_2 **g**; R^2 = 4-MeC_6H_4 **t**, Me **a**, Ph **b**

Results and Discussion

Preparation and characterisation of hydrazine complexes

Hydrazine complexes of iron(II) of the type $[Fe(R^1NHNH_2)(R^2CN)L_4][BPh_4]_2$ **1**–**3** and $[FeH(R^1NHNH_2)L_4]BPh_4$ **4** were prepared by treating nitrile compounds $[Fe(R^2CN)_2L_4][BPh_4]_2$ and $[FeH(R^2CN)L_4]BPh_4$ with an excess of the appropriate hydrazine, as shown in Scheme 1.

The $[Fe(R^1NHNH_2)(R^2CN)L_4][BPh_4]_2$ derivatives described are numbered as given above (Table 1), additionally denoted to indicate the specific substituent of the hydrazine R^1. The substitution of the nitrile groups in $[Fe(R^2CN)_2L_4]^{2+}$ cations takes place also with disubstituted hydrazines such as the *N*,*N*-dimethylhydrazine affording the corresponding $[Fe(Me_2NNH_2)(R^2CN)L_4][BPh_4]_2$ **1tg** derivative. Furthermore, the substitution rate of the R^2CN ligand with R^1NHNH_2 in the $[FeH(R^2CN)L_4]^+$ cation is very low, in the case of L = $PPh(OEt)_2$, thereby preventing the isolation of pure samples of the hydrazine complexes.

Good analytical data were obtained for all the complexes **1**–**4** which are yellow, diamagnetic solids stable in the air and in solutions of polar organic solvents where they behave as 2 : 1 (**1**–**3**) and 1 : 1 (**4**) electrolytes.[14] Diagnostic for the presence of the hydrazine ligand were both the infrared and the ^1H NMR data some of which are reported in Table 2. The infrared spectra show in the 3396–3220 cm^{-1} region three or four weak bands due to the ν(NH) frequencies of the R^1NHNH_2 ligand, while the related δ(NH_2) appear at 1594–1642 cm^{-1}. Furthermore, in the spectra of the *p*-toluonitrile complexes **1t** and **3t** the ν(CN) band is also observed at 2255–2239 cm^{-1}. For the $[FeH(RNHNH_2)L_4]^+$ **4** derivatives the ν(FeH) absorption appears at 1874–1877 cm^{-1}. However, further support for the presence of the hydrazine ligand in **1**–**4** comes from the ^1H NMR spectra which show the characteristic RNH and NH_2 signals between δ 6.31 and 4.60 for the nitrilehydrazine complexes **1**–**3** and between δ 5.95 and 2.87 for the $[FeH(R^1NHNH_2)L_4]BPh_4$ derivatives. The correct assignment has been obtained by accurate integration of the signals and homodecoupling experiments. The results also show that, in the case of the NH_2NH_2 complexes, two NH_2 ^1H NMR signals are present for all the complexes, suggesting the presence of an η^1 coordination for the hydrazine ligand. Furthermore, in the high-field region of the ^1H NMR spectra of $[FeH(R^1NHNH_2)L_4]^+$ **4** cations the hydride ligand is also observed as a multiplet at

Table 2 Infrared and NMR data for the iron(II) complexes

	IR^b		^{1}H NMR^{c,d}		^{31}P-{^{1}H} NMR^{d,e}	
Compound^a	$\tilde{\nu}$/cm^{-1}	Assignment	δ	Assignment	Spin system	δ, *J*/Hz
1ta [Fe(NH$_2$NH$_2$)(4-MeC$_6$H$_4$CN){P(OEt)$_3$}$_4$]$^{2+}$	3399, 3356, 3298, 3266w	ν(NH)	6.12 (br)	FeNH$_2$	AB$_2$C	$\delta_{\rm A}$ 163.3
	2236w	ν(CN)	5.09 (br)	NH$_2$		$\delta_{\rm B}$ 160.8
	1625, 1613m	δ(NH$_2$)	4.20–3.80 (m)	POCH_2CH$_3$		$\delta_{\rm C}$ 160.7
			2.42 (s)	CH_3C$_6$H$_4$		$J_{\rm AB}$ 153.5
			1.31, 1.29, 1.13 (t)	POCH$_2$CH_3		$J_{\rm AC}$ 142.5
						$J_{\rm BC}$ 149.5
1tc [Fe(PhNHNH$_2$)(4-MeC$_6$H$_4$CN){P(OEt)$_3$}$_4$]$^{2+}$	3360, 3305, 3245w	ν(NH)	5.50 (t)^f	RNH	ABC$_2^f$	$\delta_{\rm A}$ 157.3
	2249w	ν(CN)	5.34 (m)	NH$_2$		$\delta_{\rm B}$ 151.4
	1601m	δ(NH$_2$)	4.44–4.28 (m)	POCH_2CH$_3$		$\delta_{\rm C}$ 143.6
			2.44 (s)	CH_3C$_6$H$_4$		$J_{\rm AB}$ 142.3
			1.40, 1.39, 1.32 (t)	POCH$_2$CH_3		$J_{\rm AC}$ 127.6
						$J_{\rm BC}$ 141.8
1td [Fe(4-MeC$_6$H$_4$NHNH$_2$)(4-MeC$_6$H$_4$CN){P(OEt)$_3$}$_4$]$^{2+}$	3358, 3306, 3245w	ν(NH)	5.38 (m)^f	RNH	ABC$_2^f$	$\delta_{\rm A}$ 157.3
	2249w	ν(CN)	5.31 (m)	NH$_2$		$\delta_{\rm B}$ 151.5
	1603m	δ(NH$_2$)	4.55–4.33 (m)	POCH_2CH$_3$		$\delta_{\rm C}$ 143.7
			2.47 (s)	CH_3C$_6$H$_4$CN		$J_{\rm AB}$ 141.9
			2.27 (s)	CH_3C$_6$H$_4$NH		$J_{\rm AC}$ 127.3
			1.46, 1.44, 1.37 (t)	POCH$_2$CH_3		$J_{\rm BC}$ 141.7
1te [Fe(4-ClC$_6$H$_4$NHNH$_2$)(4-MeC$_6$H$_4$CN){P(OEt)$_3$}$_4$]$^{2+}$	3364, 3299, 3245w	ν(NH)	5.68 (t)^f	RNH	ABC$_2^f$	$\delta_{\rm A}$ 157.1
	2255w	ν(CN)	5.37 (m)	NH$_2$		$\delta_{\rm B}$ 151.3
	1604m	δ(NH$_2$)	4.45–4.25 (m)	POCH_2CH$_3$		$\delta_{\rm C}$ 143.4
			2.45 (s)	CH_3C$_6$H$_4$CN		$J_{\rm AB}$ 143.0
			1.42, 1.37, 1.36 (t)	POCH$_3$CH_3		$J_{\rm AC}$ 128.6
						$J_{\rm BC}$ 140.8
1tg [Fe(Me$_2$NNH$_2$)(4-MeC$_6$H$_4$CN){P(OEt)$_3$}$_4$]$^{2+}$	3307w	ν(NH)	4.60–4.25 (m)^f	POCH_2CH$_3$	ABC$_2^f$	$\delta_{\rm A}$ 157.8
	2250w	ν(CN)	2.67 (s)	NCH$_3$		$\delta_{\rm B}$ 150.3
	1604m	δ(NH$_2$)	2.49 (s)	CH_3C$_6$H$_4$		$\delta_{\rm C}$ 143.9
			1.44, 1.43 (t)	POCH$_2$CH_3		$J_{\rm AB}$ 132.5
						$J_{\rm AC}$ 128.6
						$J_{\rm BC}$ 144.8
3ta [Fe(NH$_2$NH$_2$)(4-MeC$_6$H$_4$CN){PPh(OEt)$_2$}$_4$]$^{2+}$	3388, 3300, 3263w	ν(NH)	6.10 (br)	FeNH$_2$	A$_2$BC	$\delta_{\rm A}$ 196.7
	2251w	ν(CN)	5.35 (br)	NH$_2$		$\delta_{\rm B}$ 194.8
	1603m	δ(NH$_2$)	4.20–3.60 (m)	POCH_2CH$_3$		$\delta_{\rm C}$ 192.4
			2.40 (s)	CH_3C$_6$H$_4$		$J_{\rm AB}$ 88.3
			1.45–1.10 (m)	POCH$_2$CH_3		$J_{\rm AC}$ 100.5
						$J_{\rm BC}$ 103.7
3tb [Fe(MeNHNH$_2$)(4-MeC$_6$H$_4$CN){PPh(OEt)$_2$}$_4$]$^{2+}$	3347, 3281, 3221w	ν(NH)	4.20 (m)	NH$_2$	ABC$_2^f$	$\delta_{\rm A}$ 188.8
	2249w	ν(CN)	4.10–3.50 (m)	POCH_2CH$_3$		$\delta_{\rm B}$ 183.8
	1603m	δ(NH$_2$)	2.41 (d)	NCH$_3$		$\delta_{\rm C}$ 177.8
			2.33 (s)	CH_3C$_6$H$_4$		$J_{\rm AB}$ 100.2
			2.24 (m)	RNH		$J_{\rm AC}$ 90.7
			1.37, 1.35, 1.32, 1.26 (t)	POCH$_2$CH_3		$J_{\rm BC}$ 102.9
3tc [Fe(PhNHNH$_2$)(4-MeC$_6$H$_4$CN){PPh(OEt)$_2$}$_4$]$^{2+}$	3386, 3283w	ν(NH)	4.99 (m)^f	NH$_2$	ABC$_2^f$	$\delta_{\rm A}$ 189.7
	2239w	ν(CN)	4.91 (m)	RNH		$\delta_{\rm B}$ 183.0
	1601m	δ(NH$_2$)	4.30–3.70 (m)	POCH_2CH$_3$		$\delta_{\rm C}$ 177.7
			2.37 (s)	CH_3C$_6$H$_4$		$J_{\rm AB}$ 103.6
			1.51, 1.48, 1.36, 1.11 (t)	POCH$_2$CH_3		$J_{\rm AC}$ 88.9
						$J_{\rm BC}$ 103.6
3td [Fe(4-MeC$_6$H$_4$NHNH$_2$)(4-MeC$_6$H$_4$CN){PPh(OEt)$_2$}$_4$]$^{2+}$	3375, 3285w	ν(NH)	4.97 (m)^f	NH$_2$	ABC$_2^f$	$\delta_{\rm A}$ 189.8
	2240w	ν(CN)	4.80 (m)	RNH		$\delta_{\rm B}$ 183.1
	1602m	δ(NH$_2$)	4.30–3.70 (m)	POCH_2CH$_3$		$\delta_{\rm C}$ 177.8
			2.37 (s)	CH_3C$_6$H$_4$CN		$J_{\rm AB}$ 103.7
			2.29 (s)	CH_3C$_6$H$_4$NH		$J_{\rm AC}$ 88.3
			1.52, 1.47, 1.36, 1.11 (t)	POCH$_2$CH_3		$J_{\rm BC}$ 103.5
1aa [Fe(NH$_2$NH$_2$)(MeCN){P(OEt)$_3$}$_4$]$^{2+}$	3396, 3354, 3313, 3264w	ν(NH)	5.39 (br)	FeNH$_2$	AB$_2$C	$\delta_{\rm A}$ 163.24
	1639m	δ(NH$_2$)	4.81 (br)	NH$_2$		$\delta_{\rm B}$ 161.32
			4.10–3.80 (m)	POCH_2CH$_3$		$\delta_{\rm C}$ 161.26
			1.60 (s)	CH$_3$CN		$J_{\rm AB}$ 151.0
			1.30, 1.27, 1.21 (t)	POCH$_2$CH_3		$J_{\rm AC}$ 142.0
						$J_{\rm BC}$ 150.0
1ad [Fe(4-MeC$_6$H$_4$NHNH$_2$)(MeCN){P(OEt)$_3$}$_4$]$^{2+}$	3366, 3305, 3248m	ν(NH)	5.20 (m)^f	RNHNH_2	ABC$_2^f$	$\delta_{\rm A}$ 157.6
	1610m	δ(NH$_2$)	4.50–4.20 (m)	POCH_2CH$_3$		$\delta_{\rm B}$ 152.4
			2.26 (s)	CH_3C$_6$H$_4$NH		$\delta_{\rm C}$ 144.5
			2.08 (s)	CH$_3$CN		$J_{\rm AB}$ 141.7
			1.40, 1.39, 1.37 (t)	POCH$_2$CH_3		$J_{\rm AC}$ 126.9
						$J_{\rm BC}$ 142.0
1af [Fe(4-O$_2$NC$_6$H$_4$NHNH$_2$)(MeCN){P(OEt)$_3$}$_4$]$^{2+}$	3387, 3320, 3292m	ν(NH)	6.31 (t, br)	RNH	ABC$_2^f$	$\delta_{\rm A}$ 163.9
	1604m	δ(NH$_2$)	4.20–3.50 (m)	POCH_2CH$_3$		$\delta_{\rm B}$ 160.9
			1.74 (s)	CH$_3$CN		$\delta_{\rm C}$ 143.2
			1.35–1.20 (m)	POCH$_2$CH_3		$J_{\rm AB}$ 120.1
						$J_{\rm AC}$ 144.6
						$J_{\rm BC}$ 122.5
2aa [Fe(NH$_2$NH$_2$)(MeCN){P(OMe)$_3$}$_4$]$^{2+}$	3391, 3327, 3313, 3246w	ν(NH)	5.41 (br)	FeNH$_2$		171–143
	1642m	δ(NH$_2$)	4.67 (br)	NH$_2$		(m)
			3.60 (m)	POCH$_3$		
			1.60 (s)	CH$_3$CN		

Table 2 (*Continued*)

Compound[a]	IR[b]		^{1}H NMR[c,d]		^{31}P-{^{1}H} NMR[d,e]	
	ν̃/cm^{-1}	Assignment	δ	Assignment	Spin system	δ, *J*/Hz
2ac $[\mathrm{Fe(PhNHNH_2)(MeCN)}\{\mathrm{P(OMe)_3}\}_4]^{2+}$	3375, 3303, 3250w	ν(NH)	5.45 (t)[f]	$\mathrm{NH_2}$	$\mathrm{ABC_2}$[f]	δ_A 162.7
	1601m	δ($\mathrm{NH_2}$)	5.24 (m)	RNH		δ_B 157.7
			4.00–3.80 (m)	$\mathrm{POCH_3}$		δ_C 148.6
			2.44 (s)	$\mathrm{CH_3CN}$		J_{AB} 143.4
						J_{AC} 129.1
						J_{BC} 141.7
3ac $[\mathrm{Fe(PhNHNH_2)(MeCN)}\{\mathrm{PPh(OEt)_2}\}_4]^{2+}$	3375, 3283, 3224m	ν(NH)	4.75 (m, br)[f]	$\mathrm{RN}\mathit{H}\mathrm{N}\mathit{H}_2$	$\mathrm{ABC_2}$[f]	δ_A 189.3
	1601m	δ($\mathrm{NH_2}$)	4.20–3.80 (m)	$\mathrm{POC}\mathit{H}_2\mathrm{CH_3}$		δ_B 184.9
			1.52 (t)	$\mathrm{CH_3CN}$		δ_C 177.6
			1.48–1.36 (m)	$\mathrm{POCH_2C}\mathit{H}_3$		J_{AB} 106.9
						J_{AC} 90.1
						J_{BC} 102.7
3ad $[\mathrm{Fe(4\text{-}MeC_6H_4NHNH_2)(MeCN)}\{\mathrm{PPh(OEt)_2}\}_4]^{2+}$	3376, 3285, 3222w	ν(NH)	4.76 (m)[f]	$\mathrm{NH_2}$	$\mathrm{ABC_2}$[f]	δ_A 189.5
	1606m	δ($\mathrm{NH_2}$)	4.68 (m)	RNH		δ_B 185.0
			4.30–3.80 (m)	$\mathrm{POC}\mathit{H}_2\mathrm{CH_3}$		δ_C 177.8
			2.27 (s)	$\mathrm{C}\mathit{H}_3\mathrm{C_6H_4}$		J_{AB} 106.0
			1.57 (t)	$\mathrm{CH_3CN}$		J_{AC} 89.9
			1.50–1.07 (m)	$\mathrm{POCH_2C}\mathit{H}_3$		J_{BC} 102.6
1ba $[\mathrm{Fe(NH_2NH_2)(PhCN)}\{\mathrm{P(OEt)_3}\}_4]^{2+}$	3397, 3345, 3305, 3265w	ν(NH)	6.18 (br)[f]	$\mathrm{NH_2}$	$\mathrm{AB_2C}$[f]	δ_A 163.26
	1604m	δ($\mathrm{NH_2}$)	5.12 (br)	$\mathrm{FeNH_2}$		δ_B 160.62
			4.20–3.75 (m)	$\mathrm{POC}\mathit{H}_2\mathrm{CH_3}$		δ_C 160.40
			1.30, 1.11 (t)	$\mathrm{POCH_2C}\mathit{H}_3$		J_{AB} 153.0
						J_{AC} 138.0
						J_{BC} 150.0
4a $[\mathrm{FeH(NH_2NH_2)}\{\mathrm{P(OEt)_3}\}_4]^{+}$	3373, 3331, 3269w	ν(NH)	4.15–3.78 (m)	$\mathrm{POC}\mathit{H}_2\mathrm{CH_3}$	$\mathrm{AB_2C}$	δ_A 175.1
	1874w (br)	ν(FeH)	3.63 (m)	$\mathrm{FeNH_2}$		δ_B 167.9
	1594w	δ($\mathrm{NH_2}$)	2.87 (m)	$\mathrm{NH_2}$		δ_C 161.5
			1.30, 1.23, 1.19 (t)	$\mathrm{POCH_2C}\mathit{H}_3$		J_{AB} 130.5
			−9.44 to −10.46 (m)	FeH		J_{AC} 82.8
						J_{BC} 68.8
4c $[\mathrm{FeH(PhNHNH_2)}\{\mathrm{P(OEt)_3}\}_4]^{+}$	3368, 3314, 3248w	ν(NH)	5.00 (t, br)[f]	RNH	$\mathrm{AB_2C}$[f]	δ_A 176.5
	1877w (br)	ν(FeH)	4.45 (m)	$\mathrm{NH_2}$		δ_B 167.9
	1603w	δ($\mathrm{NH_2}$)	4.35–3.90 (m)	$\mathrm{POC}\mathit{H}_2\mathrm{CH_3}$		δ_C 162.2
			1.35, 1.29, 1.22 (t)	$\mathrm{POCH_2C}\mathit{H}_3$		J_{AB} 131.7
			−8.85 to −10.12 (m)	FeH		J_{AC} 81.7
						J_{BC} 72.3
4d $[\mathrm{FeH(4\text{-}MeC_6H_4NHNH_2)}\{\mathrm{P(OEt)_3}\}_4]^{+}$	3370, 3306, 3242w	ν(NH)	4.87 (t, br)[f]	RNH	$\mathrm{AB_2C}$[f]	δ_A 176.6
	1874w (br)	ν(FeH)	4.37 (br)	$\mathrm{NH_2}$		δ_B 168.1
	1617w	δ($\mathrm{NH_2}$)	4.30–3.90 (m)	$\mathrm{POC}\mathit{H}_2\mathrm{CH_3}$		δ_C 162.4
			2.39 (s)	$\mathrm{C}\mathit{H}_3\mathrm{C_6H_4}$		J_{AB} 131.4
			1.34, 1.25, 1.22 (t)	$\mathrm{POCH_2C}\mathit{H}_3$		J_{AC} 81.8
			−8.85 to −10.11 (m)	FeH		J_{BC} 72.2
4f $[\mathrm{FeH(4\text{-}O_2NC_6H_4NHNH_2)}\{\mathrm{P(OEt)_3}\}_4]^{+}$	3387, 3302w	ν(NH)	5.95 (t, br)[f]	RNH	$\mathrm{AB_2C}$[f]	δ_A 176.1
	1874w	ν(FeH)	4.64 (m, br)	$\mathrm{NH_2}$		δ_B 167.1
	1602m	δ($\mathrm{NH_2}$)	4.35–3.90 (m)	$\mathrm{POC}\mathit{H}_2\mathrm{CH_3}$		δ_C 161.6
			1.35, 1.25, 1.22 (t)	$\mathrm{POCH_2C}\mathit{H}_3$		J_{AB} 134.0
			−8.78 to −10.04 (m)	FeH		J_{AC} 84.2
						J_{BC} 71.7
5 $[\mathrm{Fe(\eta^2\text{-}PhCONHNH_2)}\{\mathrm{P(OEt)_3}\}_4]^{2+}$	3284, 3212w	ν(NH)	6.50 (m)[g]	$\mathrm{NH_2}$	$\mathrm{AB_2C}$	δ_A 160.8
	1636s	ν(CO)	6.16 (br)	RNH		δ_B 159.3
	1602m	δ($\mathrm{NH_2}$)	4.10–3.80 (m)	$\mathrm{POC}\mathit{H}_2\mathrm{CH_3}$		δ_C 141.4
			1.23, 1.14, 1.12 (t)	$\mathrm{POCH_2C}\mathit{H}_3$		J_{AB} 133.7
						J_{AC} 132.2
						J_{BC} 135.8
6ta $[\mathrm{Fe}\{\eta^2\text{-}\mathrm{NH{=}C(4\text{-}MeC_6H_4)NHNH_2}\}\{\mathrm{P(OEt)_3}\}_4]^{2+}$	3394, 3336, 3305w	ν(NH)	6.48 (br), 9.47 (br)[f]	HN=	$\mathrm{AB_2C}$	δ_A 162.6
	1632m	δ($\mathrm{NH_2}$)	5.65 (br), 6.21 (br)[f]	RNH		δ_B 160.1
			5.45 (t, br), 6.48 (t, br)[f]	$\mathrm{NH_2}$		δ_C 141.6
			4.13–3.90 (m)	$\mathrm{POC}\mathit{H}_2\mathrm{CH_3}$		J_{AB} 117.9
			2.39 (s)	$\mathrm{C}\mathit{H}_3\mathrm{C_6H_4}$		J_{AC} 142.9
			1.34, 1.23 (t)	$\mathrm{POCH_2C}\mathit{H}_3$		J_{BC} 123.0
6aa $[\mathrm{Fe}\{\eta^2\text{-}\mathrm{NH{=}C(Me)NHNH_2}\}\{\mathrm{P(OEt)_3}\}_4]^{2+}$	3399, 3346, 3303w	ν(NH)	8.95 (br)[f]	HN=	$\mathrm{ABC_2}$[f]	δ_A 165.3
	1645m	δ($\mathrm{NH_2}$)	6.27 (t, br)	$\mathrm{NH_2}$		δ_B 161.8
			6.19 (br)	RNH		δ_C 144.2
			4.35 (m)	$\mathrm{POC}\mathit{H}_2\mathrm{CH_3}$		J_{AB} 120.1
			2.17 (s)	$\mathrm{CCH_3}$		J_{AC} 141.8
			1.38, 1.35 (t)	$\mathrm{POCH_2C}\mathit{H}_3$		J_{BC} 122.5
6ba $[\mathrm{Fe}\{\eta^2\text{-}\mathrm{NH{=}C(Ph)NHNH_2}\}\{\mathrm{P(OEt)_3}\}_4]^{2+}$	3395, 3338, 3303w	ν(NH)	6.44 (br)	HN=	$\mathrm{ABC_2}$	δ_A 162.4
	1632m	δ($\mathrm{NH_2}$)	5.72 (br)	RNH		δ_B 160.0
			5.44 (t, br)	$\mathrm{NH_2}$		δ_C 141.6
			4.01 (m)	$\mathrm{POC}\mathit{H}_2\mathrm{CH_3}$		J_{AB} 118.7
			1.34, 1.23 (t)	$\mathrm{POCH_2C}\mathit{H}_3$		J_{AC} 142.9
						J_{BC} 122.9

Table 2 (*Continued*)

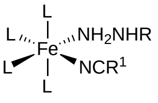
Compound[a]	IR[b] $\tilde{\nu}$/cm^{-1}	IR[b] Assignment	^{1}H NMR[c,d] δ	^{1}H NMR[c,d] Assignment	^{31}P-{^{1}H} NMR[d,e] Spin system	^{31}P-{^{1}H} NMR[d,e] δ, *J*/Hz
6tb [Fe{η^2-NH=C(4-MeC$_6$H$_4$)-	3401, 3285w	ν(NH)	5.81 (t, br), 6.56 (t, br)[f]	NH$_2$	ABC$_2$	δ_A 163.7
N(Me)NH$_2$}{P(OEt)$_3$}$_4$]$^{2+}$	1624m	δ(NH$_2$)	5.43 (br), 6.07 (br)[f]	HN=		δ_B 162.0
			4.05 (m)	POC*H*$_2$CH$_3$		δ_C 142.6
			2.82 (s)	NCH$_3$		J_{AB} 117.0
			2.44 (s)	C*H*$_3$C$_6$H$_4$		J_{AC} 144.6
			1.34, 1.32, 1.29 (t)	POCH$_2$C*H*$_3$		J_{BC} 119.6
6ab [Fe{η^2-NH=C(Me)N(Me)NH$_2$}-	3397, 3277m	ν(NH)	6.33 (t, br)[f]	NH$_2$	ABC$_2$[f]	δ_A 164.8
{P(OEt)$_3$}$_4$]$^{2+}$	1641m	δ(NH$_2$)	5.87 (br)	HN=		δ_B 162.2
			4.35–4.15 (m)	POC*H*$_2$CH$_3$		δ_C 142.7
			3.37, 2.27 (s)	CC*H*$_3$NC*H*$_3$		J_{AB} 118.0
			1.39, 1.38, 1.35 (t)	POCH$_2$C*H*$_3$		J_{AC} 145.7
						J_{BC} 119.6
7ab [Fe{η^2-NH=C(Me)N(Me)NH$_2$}-	3398, 3277w	ν(NH)	6.49 (t, br),[f] 5.41 (t, br)[d]	NH$_2$	ABC$_2$[f]	δ_A 169.1
{P(OMe)$_3$}$_4$]$^{2+}$	1638m	δ(NH$_2$)	6.27 (br), 4.99 (br)[d]	HN=		δ_B 166.8
			4.02–3.80 (m)	POCH$_3$		δ_C 147.0
			2.91, 2.26 (s)	CH$_3$		J_{AB} 119.8
						J_{AC} 147.0
						J_{BC} 119.3

[a] All complexes are BPh$_4^-$ salts. [b] In KBr pellets. [c] Phenyl proton resonances are omitted. [d] In CD$_2$Cl$_2$ at 25 °C. [e] Positive shift downfield from 85% H$_3$PO$_4$. [f] In (CD$_3$)$_2$CO at 25 °C. [g] At −70 °C.

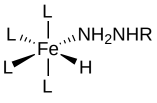
$$[Fe(R^2CN)_2L_4][BPh_4]_2 \xrightarrow{\text{excess of PhCONHNH}_2} [Fe(\eta^2\text{-PhCONHNH}_2)L_4][BPh_4]_2$$

5

Scheme 2 L = P(OEt)$_3$



I



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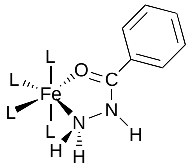


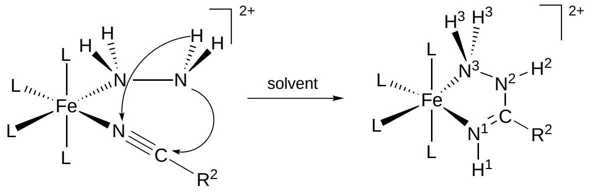
III

δ −8.78 to −10.46, consistent with the proposed formulation. Finally, a *cis* geometry of type **I** or **II** can also be proposed in solution for all the hydrazine complexes **1**–**4** on the basis of the A$_2$BC, AB$_2$C or ABC$_2$ multiplet observed in the ^{31}P-{^{1}H} NMR spectra.

Benzoylhydrazine PhCONHNH$_2$ also reacts with bis(nitrile) complexes giving substitution of both the R^{2}CN ligands and formation of the corresponding [Fe(η^2-PhCONHNH$_2$)L$_4$][BPh$_4$]$_2$ **5** complex which was isolated and characterised (Scheme 2). The infrared spectrum of the benzoylhydrazine complex **5** shows characteristic bands of the NHNH$_2$ group at 3284, 3212 [ν(NH)] and at 1602 cm^{-1} [δ(NH$_2$)] and a strong-intensity band at 1636 cm^{-1} attributable to ν(CO) of the co-ordinated carbonyl of the PhCONHNH$_2$ ligand. Of course, the band of the ν(CN) of the *p*-toluonitrile is not present. The ^{1}H NMR spectrum confirms the presence of the hydrazine ligand showing at δ 6.16 (NH) and at 6.50 (NH$_2$) the signals of the NHNH$_2$ group which are clearly attributable only at low temperature (−70 °C) owing to masking of the NH signal by the phenyl protons at room temperature. In the temperature range between +20 and −80 °C the ^{31}P-{^{1}H} NMR spectrum appears as an ABC$_2$ multiplet, consistent with the presence of a chelate benzoylhydrazine ligand of the type schematised in geometry **III**.

Table 3 Amidrazone derivatives prepared: R^1 = H **a** or Me **b**

L	R^2 4-MeC$_6$H$_4$	R^2 Me	R^2 Ph
P(OEt)$_3$	**6t**	**6a**	**6b**
P(OMe)$_3$		**7a**	



IV

1ta, **1aa**, **1ba**, **2aa** **6ta**, **6aa**, **6ba**, **7aa**

Scheme 3 L = P(OEt)$_3$ **6a** or P(OMe)$_3$ **7a**; R^2 = 4-MeC$_6$H$_4$ **t**, Ph **b** or Me **a**

Amidrazone derivatives

The behaviour in solution of the nitrilehydrazine complexes **1**–**3** depends on the nature of both the hydrazine and the ancillary phosphine ligands, as shown in Schemes 3–5. The nitrilehydrazine complexes [Fe(NH$_2$NH$_2$)(R^{2}CN)L$_4$][BPh$_4$]$_2$ containing the P(OEt)$_3$ and P(OMe)$_3$ phosphite ligands are unstable in solution and react slowly to afford new compounds which can easily be isolated and characterised as the amidrazone[15] complexes **6ta**, **6aa**, **6ba** and **7aa** of the type shown in geometry **IV**. The [Fe{η^2-NH=C(R^2)N(R^1)NH$_2$}L$_4$][BPh$_4$]$_2$ derivatives are numbered as given in Table 3, additionally denoted to indicate the specific substituent of the hydrazine R^1. The formation of these complexes can be explained (see below) according to a reaction course that involves nucleophilic attack of one end of NH$_2$NH$_2$ on the cyanide carbon atom of the co-ordinated nitrile followed by a hydrogen shift, giving a five-membered metallacycle (Scheme 3). The reaction can in fact be followed spectroscopically (by IR and NMR) and shows, in the case of [Fe(NH$_2$NH$_2$)(4-MeC$_6$H$_4$CN){P(OEt)$_3$}$_4$][BPh$_4$]$_2$ **1ta**, the disappearance of the ν(CN) band in the IR spectrum. Furthermore, in the ^{1}H NMR spectrum (CD$_2$Cl$_2$ solution), the disappearance of the two NH$_2$ signals at δ 6.12 and 5.09 of the hydrazine ligand and the appearance of three new signals at δ 6.48, 5.65 and 5.45, which integrate as 1 : 1 : 2 protons and were attributed to the H^1, H^2 and H^3 protons of the amidrazone

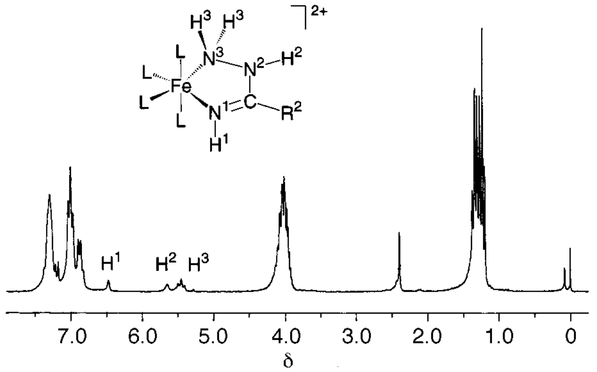


Fig. 1 Proton NMR spectrum of the compound $[Fe\{\eta^2\text{-}NH{=}C(4\text{-}MeC_6H_4)NHNH_2\}\{P(OEt)_3\}_4][BPh_4]_2$ **6ta** in CD_2Cl_2 at 25 °C

(geometry **IV**), were observed. Also the phosphite and the 4-MeC_6H_4CN ^1H signals change during the reaction course, as well as the multiplet of the ^{31}P NMR spectrum. From the solution a yellow-orange solid can be isolated in very high yield ($\geqslant$95%) the elemental analyses of which are very similar to those of the starting hydrazine complexes. Similar results were obtained for all the NH_2NH_2 complexes. Furthermore, the $[Fe(NH_2NH_2)(MeCN)\{P(OMe)_3\}_4]^{2+}$ **2aa** cation containing the $P(OMe)_3$ phosphite ligand reacts in solution to give the amidrazone complex **7aa** which, however, was isolated only as an unstable oily product. No reaction was observed for the $[Fe(NH_2NH_2)(4\text{-}MeC_6H_4CN)\{PPh(OEt)_2\}_4]^{2+}$ **3ta** cation containing the $PPh(OEt)_2$ phosphite ligand, which can be recovered unchanged after 24 h at room temperature. The use of refluxing conditions led to partial decomposition of the starting compound.

The new derivatives $[Fe\{\eta^2\text{-}NH{=}C(R^2)NHNH_2\}L_4][BPh_4]_2$ **6ta**, **6aa** and **6ba** are air-stable, diamagnetic and 1:2 electrolytes[14] and, although it was not possible to determine any crystal structure owing to the poor quality of the crystals obtained, the IR and NMR spectra (Table 2) strongly support their formulation as amidrazone complexes. The infrared spectra show three ν(NH) signals at 3401–3277 cm^{-1} reasonably attributed to the stretching of the NH_2 and NH groups, while the ν(NH) of the iminic (N^1H) group was not assigned. Furthermore, $\delta(NH_2)$ is also observed as one medium-intensity band between 1645 and 1624 cm^{-1}. Apart from the phosphites and the BPh_4^- resonances, three slightly broad signals of intensity ratio 1:1:2 are present in the ^1H NMR spectra between δ 6.48 and 5.43 (Fig. 1). These signals, whose chemical shifts change with the solvent, were assigned by homodecoupling experiments to the H^1, H^2 and H^3 protons of a chelate amidrazone ligand of the type of geometry **IV**. Such a structure is also confirmed by the $^{31}P\text{-}\{^1H\}$ NMR spectra which show, for all the compounds, an AB_2C or ABC_2 multiplet (Fig. 2).

Nucleophilic attack upon co-ordinated nitrile by alcohols, amines and carbanions to give iminoethers, amidines and imines is well established[16–18] but, to our knowledge, no example of such a type of reaction has been reported for an hydrazine molecule.[19] However, the formation in our case of the amidrazone complexes from a compound containing one nitrile and one hydrazine ligand in a mutually *cis* position seems to be plausible and represents a new example for the reaction of co-ordinated nitriles involving, for the first time, an hydrazine molecule as a reagent.

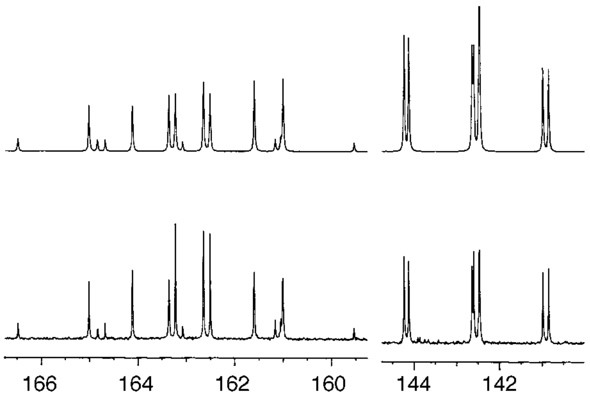
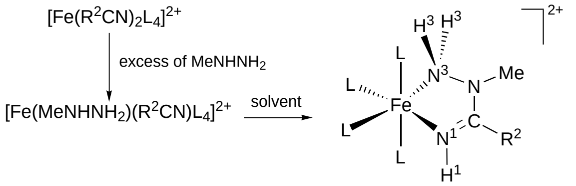


Fig. 2 Observed (bottom) and calculated (top) $^{31}P\text{-}\{^1H\}$ NMR spectra of the compound $[Fe\{\eta^2\text{-}NH{=}C(4\text{-}MeC_6H_4)N(Me)NH_2\}\{P(OEt)_3\}_4][BPh_4]_2$ **6tb** in CD_2Cl_2 at 25 °C. The simulated spectrum was obtained with the parameters reported in Table 1



6tb, **6ab**, **7aa**

Scheme 4 L = $P(OEt)_3$ **6b** or $P(OMe)_3$ **7b**; R^2 = 4-MeC_6H_4 **t** or Me **a**

Also methylhydrazine can give nucleophilic attack on the co-ordinated R^2CN ligand to give amidrazone derivatives and the reaction, in this case, is so fast even in CH_2Cl_2 as to prevent the isolation of pure samples of the hydrazine complexes $[Fe(MeNHNH_2)(R^2CN)L_4][BPh_4]_2$. From the reaction of the bis(nitrile) $[Fe(R^2CN)_2L_4][BPh_4]_2$ with $MeNHNH_2$ we always obtained a mixture of both the nitrilehydrazine and the amidrazone complexes from which only the latter $[Fe\{\eta^2\text{-}NH{=}C(R^2)N(Me)NH_2\}L_4][BPh_4]_2$ **6tb**, **6ab** and **7ab** were obtained in pure form (Scheme 4) and characterised (Table 2). The arylhydrazine complexes, instead, do not seem to give rise to the cyclisation reaction and the $[Fe(RNHNH_2)(R^2CN)L_4]^{2+}$ [R = Ph, 4-MeC_6H_4, 4-ClC_6H_4 or 4-$O_2NC_6H_4$; L = $P(OEt)_3$ or $P(OMe)_3$] derivatives can be recovered unchanged after 48 h of stirring in acetone solution. The absence of an amidrazone derivative in these cases may be explained on the basis of the steric hindrance of the aryl substituent of the co-ordinated hydrazine which seems to prevent the formation of the chelate ligand.

The cyclisation reaction giving the amidrazone complexes, however, is influenced not only by the substituent group of the hydrazine R^1NHNH_2, but also by the nature of the phosphite ligand. In fact the amidrazone complexes are formed only with the $P(OEt)_3$ and $P(OMe)_3$ ligands, while no reaction was observed with the nitrilehydrazine complexes $[Fe(NH_2NH_2)(4\text{-}MeC_6H_4CN)\{PPh(OEt)_2\}_4][BPh_4]_2$ **3ta** and $[Fe(MeNHNH_2)(4\text{-}MeC_6H_4CN)\{PPh(OEt)_2\}_4][BPh_4]_2$ **3tb** containing $PPh(OEt)_2$ as an ancillary ligand. Long reaction times or refluxing conditions caused decomposition of the starting compound **3** but did not give the cyclisation reaction. Therefore, although the number of phosphines used is limited, the results seem to indicate that a nitrile bonded to an $Fe(NH_2NHR)L_4$ fragment can undergo nucleophilic attack to the cyanide carbon atom by one end of the hydrazine only in the presence of phosphites with good π-acceptor properties,[20] such as $P(OEt)_3$ and $P(OMe)_3$. A little change in the electronic properties of the phosphine, as observed using the less π-acidic $PPh(OEt)_2$ ligand, makes the nitrile complexes unreactive toward the cyclisation reaction with all the hydrazines used, so confirming the important influence of the ancillary ligands in the cyclisation reaction.

Reactivity

The arylhydrazine complexes $[Fe(RNHNH_2)(R^2CN)L_4][BPh_4]_2$ **1** and **2** and $[FeH(RNHNH_2)\{P(OEt)_3\}_4]BPh_4$ **4** containing the $P(OEt)_3$ and $P(OMe)_3$ ligands can be oxidised by $Pb(O_2CMe)_4$

$$\underset{\mathbf{1},\,\mathbf{2}}{[\mathrm{Fe(RNHNH_2)(R^2CN)L_4}]^{2+}} \xrightarrow[-30\ ^\circ\mathrm{C}]{\mathrm{Pb(O_2CMe)_4}} [\mathrm{Fe(RN{=}NH)(R^2CN)L_4}]^{2+}$$

$\mathrm{L = P(OEt)_3}$ **8**, $\mathrm{P(OMe)_3}$ **9**

$$\underset{\mathbf{4}}{[\mathrm{FeH(RNHNH_2)\{P(OEt)_3\}_4}]^{+}} \xrightarrow[-30\ ^\circ\mathrm{C}]{\mathrm{Pb(O_2CMe)_4}} \underset{\mathbf{10}}{[\mathrm{FeH(RN{=}NH)\{P(OEt)_3\}_4}]^{+}}$$

Scheme 5 R = Ph **c** or $\mathrm{MeC_6H_4}$ **d**; $\mathrm{R^2 = 4\text{-}MeC_6H_4}$ **t** or Me **a**

to give the corresponding aryldiazene $[\mathrm{Fe(RN{=}NH)(R^2CN)L_4}][\mathrm{BPh_4}]_2$ and $[\mathrm{FeH(RN{=}NH)\{P(OEt)_3\}_4}]\mathrm{BPh_4}$ derivatives which were isolated in good yield and characterised (Scheme 5). The related $\mathrm{PPh(OEt)_2}$ complexes $[\mathrm{Fe(RNHNH_2)(R^2CN)\{PPh(OEt)_2\}_4}]^{2+}$, instead, are unreactive toward the oxidation reaction with $\mathrm{Pb(O_2CMe)_4}$ and also with other oxidising agents such as $\mathrm{H_2O_2}$ and $\mathrm{Bu^tO_2H}$.

Diagnostic for the presence of the diazene ligand in the complexes is the high-frequency signal of the NH group at δ 13–15 observed in the ^{1}H NMR spectra. However, the formulation of the oxidation products **8**–**10** is also confirmed by a comparison of their spectroscopic properties with those of the complexes $[\mathrm{Fe(RN{=}NH)(R^2CN)L_4}][\mathrm{BPh_4}]_2$ and $[\mathrm{FeH(RN{=}NH)\{P(OEt)_3\}_4}]\mathrm{BPh_4}$ previously prepared by us[6b,e] treating the hydrides $[\mathrm{FeH(R^2CN)L_4}]^+$ and $[\mathrm{FeH_2L_4}]$ with the appropriate arenediazonium $\mathrm{RN_2}^+$ cations. The identical spectroscopic properties observed in the two cases emphasise that aryldiazene complexes of iron(II) can be obtained both by insertion of an arenediazonium cation into an Fe–H bond and by oxidation of an arylhydrazine derivative of iron(II). Oxidation of hydrazine complexes giving stable diazene derivatives has been reported in a few cases[3c,21] and often involves dinuclear complexes with a diazene bridging unit.

The results obtained on the oxidation of the arylhydrazine complexes prompted us to extend these studies to the hydrazine and the methylhydrazine derivatives in an attempt to prepare the corresponding diazene NH=NH and methyldiazene MeN=NH complexes which, of course, cannot be prepared from the arenediazonium cations. Unfortunately we were not able to prepare any of these complexes by oxidation of the starting hydrazine compounds, because treating $[\mathrm{Fe(NH_2NH_2)(R^2CN)L_4}]^{2+}$ cations **1ta**, **1aa** and **2aa** $[\mathrm{L = P(OEt)_3}$ or $\mathrm{P(OMe)_3}]$ with a solution of $\mathrm{Pb(O_2CMe)_4}$ always gave the amidrazones **6** and **7** as the main product. The related complexes containing the $\mathrm{PPh(OEt)_2}$ phosphine ligand $[\mathrm{Fe(R^1NHNH_2)(R^2CN)\{PPh(OEt)_2\}_4}][\mathrm{BPh_4}]_2$ **3** ($\mathrm{R^1}$ = H or Me), instead, do not react with $\mathrm{Pb(O_2CMe)_4}$ in a stoichiometric amount at −30 °C and the use of an excess at room temperature caused only some decomposition of the starting complexes, no diazene derivative being present. The unreactivity of the hydrazine complexes containing the $\mathrm{PPh(OEt)_2}$ ligand towards the oxidation with $\mathrm{Pb(O_2CMe)_4}$ points out that also the oxidation reaction is influenced by the nature of the phosphite ligand and that only with the good π-acidic $\mathrm{P(OEt)_3}$ and $\mathrm{P(OMe)_3}$ ligands[20] the reaction with $\mathrm{Pb(O_2CMe)_4}$ can afford the corresponding diazene derivatives.

Treatment of the arylhydrazine complexes $[\mathrm{Fe(RNHNH_2)(R^2CN)\{P(OEt)_3\}_4}][\mathrm{BPh_4}]_2$ **1** with excess of triethylamine in $\mathrm{CH_2Cl_2}$ results in the formation of the ammonium salt $[\mathrm{NHEt_3}]\mathrm{BPh_4}$ and of a red solution from which, after work-up, the aryldiazenido $[\mathrm{Fe(RN_2)L_4}]\mathrm{BPh_4}$ **11** derivatives can be separated as red crystals in about 25–30% yield (Scheme 6). The related arylhydrazinenitrile complexes with the $\mathrm{PPh(OEt)_2}$ ligand $[\mathrm{Fe(RNHNH_2)(R^2CN)\{PPh(OEt)_2\}_4}][\mathrm{BPh_4}]_2$ **3** and the hydrides $[\mathrm{FeH(RNHNH_2)L_4}]\mathrm{BPh_4}$ **4**, instead, are unreactive in the presence of $\mathrm{NEt_3}$, whereas the hydrazine $\mathrm{NH_2NH_2}$ and the methylhydrazine $\mathrm{MeNHNH_2}$ complexes decompose during the treatment.

$$\underset{\mathbf{1}}{[\mathrm{Fe(RNHNH_2)(R^2CN)\{P(OEt)_3\}_4}]^{2+}} \xrightarrow[\mathrm{CH_2Cl_2}]{\text{excess of NEt}_3}$$

$$\underset{\mathbf{11}}{[\mathrm{Fe(RN_2)\{P(OEt)_3\}_4}]^{+}} + [\mathrm{NHEt_3}]^+ + \text{unidentified products}$$

Scheme 6 R = Ph, $\mathrm{4\text{-}MeC_6H_4}$ or $\mathrm{4\text{-}ClC_6H_4}$; $\mathrm{R^2 = 4\text{-}MeC_6H_4}$ or Me

The formulation of the aryldiazenido complexes $[\mathrm{Fe(RN_2)L_4}]\mathrm{BPh_4}$ is confirmed by the elemental analysis and by the spectroscopic properties (IR and NMR), which are identical to those of the $[\mathrm{Fe(RN_2)L_4}]\mathrm{BPh_4}$ complexes previously prepared by us[6b] by deprotonation with $\mathrm{NEt_3}$ of the bis(aryldiazene) $[\mathrm{Fe(RN{=}NH)_2L_4}][\mathrm{BPh_4}]_2$ derivatives. The formation of an aryldiazenido complex from an arylhydrazine derivative is rather surprising also in view of the fact that the final complex contains a two-electron-reduced metal centre[6b] ($\mathrm{Fe^0}$) and a four-electron oxidised ligand ($\mathrm{RN_2}^+$) with respect to the starting derivative. Therefore we have studied this reaction by IR and NMR spectroscopy in order to detect possible intermediates and to propose a probable reaction pathway.

Monitoring the progress of the reaction by IR spectra one can observe the disappearance of the ν(CN) band at 2255–2249 cm^{-1} and the appearance of the 2230 cm^{-1} absorption of the free nitrile $\mathrm{4\text{-}MeC_6H_4CN}$. The formation of free nitrile is quantitative. No other new band, apart from that of ν($\mathrm{N_2}$) of the final $[\mathrm{Fe(RN_2)L_4}]^+$ cations at 1650–1640 cm^{-1}, was observed. From the reaction mixture we separated a white solid characterised as $[\mathrm{NHEt_3}]\mathrm{BPh_4}$ and present in a ratio $[\mathrm{NHEt_3}]^+$: Fe greater than 1 : 1 (1.3 : 1–1.4 : 1). Unfortunately, the ^{1}H and ^{31}P NMR spectra of the reaction mixture do not give any conclusive information, showing only rather broad signals, probably due to the formation of paramagnetic intermediates. Therefore we cannot propose any reaction path for this complicated reaction that proceeds with loss of the nitrile ligand and a concurrent deprotonation affording, as final product, the aryldiazenido $[\mathrm{Fe(RN_2)L_4}]\mathrm{BPh_4}$ complex. Taking into account the low yield observed (below 50%) and that the final product contains a two-electron-reduced metal and a four-electron-oxidised ligand, one may suspect a disproportionation reaction which, however, must still be confirmed.

Acknowledgements

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