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Preparation and reactivity towards hydrazines of bis(cyanamide) and bis(cyanoguanidine) complexes of the iron triad†

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Bis(diethylcyanamide) $[Fe(N{\equiv}CNEt_2)_2L_4](BPh_4)_2$ **1a** and bis(cyanoguanidine) $[Fe\{N{\equiv}CN(H)C(NH_2){=}NH\}_2L_4](BPh_4)_2$ **1b** [L = $P(OEt)_3$] complexes were prepared by allowing iron(II) chloride to react first with an excess of $P(OEt)_3$ and then of the appropriate cyanamide, followed by addition of an excess of $NaBPh_4$. Instead, bis(complexes) of ruthenium and osmium $[M(N{\equiv}CNEt_2)_2L_4](BPh_4)_2$ **2a**, **3a** and $[M\{N{\equiv}CN(H)C(NH_2){=}NH\}_2L_4](BPh_4)_2$ **2b**, **3b** (M = Ru **2**, Os **3**) were prepared by reacting hydrides MH_2L_4 first with either triflic acid HOTf or methyltriflate MeOTf and then with an excess of the appropriate cyanamide. Hydride-diethylcyanamide $[MH(N{\equiv}CNEt_2)L_4]BPh_4$ **4a**, **5a** and hydride-cyanoguanidine complexes $[MH\{N{\equiv}CN(H)C(NH_2){=}NH\}L_4](BPh_4)_2$ **4b**, **5b** (M = Ru **4**, Os **5**) were also obtained by reacting MH_2L_4 first with one equivalent of HOTf or MeOTf and then with the appropriate cyanamide. Treatment of bis(cyanamide) and bis(cyanoguanidine) complexes **1–3** with hydrazines $RNHNH_2$ afforded hydrazinecarboximidamide derivatives $[M\{\eta^2\text{-}N(H){=}C(NEt_2)N(R)NH_2\}L_4](BPh_4)_2$ **6a–12a** and $[M\{\eta^2\text{-}N(H){=}C[N{=}C(NH_2)_2]N(R)NH_2\}L_4](BPh_4)_2$ **6b–12b** (M = Fe **6–8**, Ru **9**, **10**, Os **11**, **12**; R = H **6**, **9**, **11**, Me **7**, **10**, **12**, Ph **8**). A reaction path involving nucleophilic attack by hydrazine on the cyanamide carbon atom is proposed. All the complexes were characterised by spectroscopy and X-ray crystal structure determination of $[Os\{\eta^2\text{-}NH{=}C[N{=}C(NH_2)_2]N(CH_3)NH_2\}\{P(OEt)_3\}_4](BPh_4)_2$ **12b**.

Introduction

The chemistry of transition metal complexes containing either cyanamides $N{\equiv}CNR_2$ (R = H, alkyl, aryl) or the related cyanoguanidine $N{\equiv}CN(H)C(NH_2){=}NH$ as ligands[1–8] has been far less developed than that of organonitriles RCN,[9,10] in spite of the synthetic and biological interest of these amino-functionalised nitrile species. They are in fact used as precursors in the synthesis[11] of polymers, fertilisers, pesticides and pharmaceuticals, and have biological importance[9b,12] as substrates of both Mo and V nitrogenases and cyanamide hydrate and as a histamine H_2-receptor antagonist.

Relatively few papers on the synthesis and reactivity of cyanamide and cyanoguanidine complexes of transition metals have recently been reported,[1–8] mainly involving molybdenum,[7] platinum[6] and copper[5] as metal centres. There are interesting studies on nucleophilic addition to the metal-activated CN triple bond of cyanoguanidine, reported for Cu, Ni and Pt,[13] and amination of Pt-bonded cyanoguanidine.[6f]

We are interested in the chemistry of azo complexes of the iron triad and have reported the synthesis of not only diazene and hydrazine derivatives,[14] but also amidrazone complexes obtained by nucleophilic attack of hydrazine on the coordinate nitrile.[15] Recently, extension to cyanamide ligands allowed us to prepare diethylcyanamide and cyanoguanidine complexes of Ru and Os stabilised by half-sandwich *p*-cymene fragments.[16] Now, as a continuation of the above studies, we report the preparation of the first bis(diethylcyanamide) and bis(cyanoguanidine) complexes of the iron triad and their reactivity with hydrazines, affording new triaza derivatives.

Experimental

General comments

All reactions were carried out in an inert atmosphere (argon) by means of standard Schlenk techniques or in an inert-atmosphere glove box. Once isolated, the complexes were found to be relatively stable in air. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $RuCl_3{\cdot}3H_2O$ and OsO_4 were

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Pressure Chemical Co. (USA) products, and used as received. Triethylphosphite $P(OEt)_3$ was an Aldrich product, purified by distillation under nitrogen. Hydrazine NH_2NH_2 was prepared by decomposition of hydrazine cyanurate (Fluka) by following the reported method.[17] Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra were obtained on an AVANCE 300 Bruker spectrometer (^1H, 300 MHz; ^{31}P, 121.52 MHz; ^{13}C, 75.48 MHz) at temperatures between +20 and −80 °C, unless otherwise noted. ^1H and $^{13}C\{^1H\}$ spectra are referenced to internal tetramethylsilane; $^{31}P\{^1H\}$ chemical shifts are reported with respect to 85% H_3PO_4; downfield shifts are considered positive; J values are given in Hz. COSY, HMQC and HMBC NMR experiments were performed with standard programs. The iNMR software package[18] was used to process NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C was measured on a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze del Farmaco, University of Padova (Italy).

Synthesis of complexes

Hydrides $RuH_2[P(OEt)_3]_4$ and $OsH_2[P(OEt)_3]_4$ were prepared following the known method.[19,20]

$[Fe(N{\equiv}CNEt_2)_2\{P(OEt)_3\}_4](BPh_4)_2$ 1a

An excess of $P(OEt)_3$ (12.5 mmol, 2.1 cm^3) was added to a solution of anhydrous $FeCl_2$ (2.5 mmol, 0.32 g) in 25 cm^3 of ethanol and the reaction mixture refluxed for 90 min. An excess of diethylcyanamide $N{\equiv}CNEt_2$ (12.5 mmol, 1.45 cm^3) was added to the solution, brought to room temperature and the mixture stirred for 3 h. The addition of an excess of $NaBPh_4$ (6.2 mmol, 2.12 g) in ethanol (5 cm^3) to the resulting solution caused the separation of a yellow solid, which was filtered and crystallised from dichloromethane CH_2Cl_2 and ethanol; yield ≥75%. (^1H NMR (CD_2Cl_2, 25 °C) δ: 7.73–6.90 (m, 40H, Ph), 4.16 (s), 4.03 (m) (24H, CH_2 phos), 3.88 (q, 8H, CH_2 NEt), 1.38, 1.30 (t, 36H, CH_3 phos), 1.21 (t, 12H, CH_3 NEt); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2B_2 spin syst, δ_A 155.4, δ_B 142.3, J_{AB} = 142.8. IR (KBr)/cm^{-1}: 2264 (m) $\nu_{C{\equiv}N}$. Λ_M/S cm^2 mol^{-1} = 115. Found: C, 63.48; H, 7.86; N, 3.51. $C_{82}H_{120}B_2FeN_4O_{12}P_4$ (1555.21) requires C, 63.33; H, 7.78; N, 3.60%.)

$[Fe\{N{\equiv}CN(H)C(NH_2){=}NH\}_2\{P(OEt)_3\}_4](BPh_4)_2$ 1b

An excess of $P(OEt)_3$ (12.5 mmol, 2.1 cm^3) was added to a solution of anhydrous $FeCl_2$ (2.5 mmol, 0.32 g) in ethanol (15 cm^3) and the reaction mixture was refluxed for 90 min. An excess of cyanamide $N{\equiv}CNH_2$ (12.5 mmol, 0.53 g) in ethanol (5 cm^3) was added to the solution brought to room temperature and the mixture stirred for 3 h. Alternatively, an excess of cyanoguanidine $N{\equiv}CN(H)C(NH_2){=}NH$ (6.0 mmol, 0.50 g) in ethanol (5 cm^3) was added to the solution brought to room temperature and the mixture stirred for 3 h. The addition of an excess of $NaBPh_4$ (6.2 mmol, 2.12 g) in ethanol (5 cm^3) caused the separation of a yellow solid, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥80%. (^1H NMR (CD_2Cl_2, 25 °C) δ: 7.40–6.94 (m, 40H, Ph), 4.24 (br, 8H, NH + NH_2), 4.09, 3.98 (m, 24H, CH_2), 1.32, 1.26 (t, 36H, CH_3); (−70 °C) 5.14, 3.53 (br, 4H, NH), 3.34 (br, 4H, NH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2B_2, δ_A 129.7, δ_B 121.8, J_{AB} = 59.5. IR (KBr)/cm^{-1}: 3440, 3350 (s) ν_{NH}; 2247 (s) $\nu_{C{\equiv}N}$; 1631 (s) δ_{NH_2}. Λ_M/S cm^2 mol^{-1} = 122. Found: C, 59.95; H, 7.04; N, 7.25. $C_{76}H_{108}B_2FeN_8O_{12}P_4$ (1527.08) requires C, 59.78; H, 7.13; N, 7.34%.)

$[Ru(N{\equiv}CNEt_2)_2\{P(OEt)_3\}_4](BPh_4)_2$ 2a and $[Ru\{N{\equiv}CN(H)C(NH_2){=}NH\}_2\{P(OEt)_3\}_4](BPh_4)_2$ 2b

In a 25 cm^3 three-necked round-bottomed flask were placed 0.20 g (0.26 mmol) of $RuH_2[P(OEt)_3]_4$ and 7 cm^3 of toluene. An equimolar amount of triflic acid $HOSO_2CF_3$ (HOTf) (0.26 mmol, 23 μL) was added to the solution cooled to −196 °C and the reaction mixture brought to room temperature and stirred for 1 h. Another equimolar amount of HOTf (0.26 mmol, 23 μL) was further added to the solution cooled to −196 °C and the reaction mixture, brought to room temperature, stirred for 1 h. An excess of the appropriate cyanamide $N{\equiv}CNEt_2$ (0.78 mmol, 90 μL) or $N{\equiv}CNH_2$ (1.6 mmol, 67 mg) in ethanol (5 cm^3) was added and the resulting solution stirred for 2 h. The solvent was removed under reduced pressure giving an oil, which was triturated with ethanol (3 cm^3) containing an excess of $NaBPh_4$ (0.78 mmol, 0.27 g). A white solid slowly separated out by cooling the resulting solution to −25 °C, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥65%. (**2a**: ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.33–6.70 (m, 40 H, Ph), 4.32, 4.25 (m, 24 H, CH_2 phos), 3.37 (q, 8 H, CH_2 NEt), 1.40, 1.38 (t, 36 H, CH_3 phos), 1.35 (t, 12 H, CH_3 NEt). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: A_2B_2, δ_A 130.0, δ_B 120.5, J_{AB} = 60.8. IR (KBr)/cm^{-1}: 2264 (m) $\nu_{C{\equiv}N}$. Λ_M/S cm^2 mol^{-1} = 125. Found: C, 61.31; H, 7.68; N, 3.39. $C_{82}H_{120}B_2N_4O_{12}P_4Ru$ (1600.44) requires C, 61.54; H, 7.56; N, 3.50%. **2b**: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.38–6.86 (m, 40 H, Ph), 4.16 (br, 8 H, NH + NH_2), 4.03, 3.98 (m, 24 H, CH_2), 1.29, 1.26 (t, 36 H, CH_3); (−30 °C) 4.46 (br, 4 H, NH), 3.65 (br, 4 H, NH_2); (−70 °C) 5.10, 3.56 (br, 4 H, NH), 3.25 (br, 4 H, NH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 165–122.5 (m, Ph), 162.22 (s, CNH_2), 121.9 (t, C≡N), 63.10 (m, CH_2), 16.41 (m, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2B_2, δ_A 131.1, δ_B 121.7, J_{AB} = 60.8. IR (KBr)/cm^{-1}: 3435, 3356 (s), 3233 (w) ν_{NH}; 2246 (s) $\nu_{C{\equiv}N}$; 1630 (s) δ_{NH_2}. Λ_M/S cm^2 mol^{-1} = 119. Found: C, 57.85; H, 6.82; N, 7.26. $C_{76}H_{108}B_2N_8O_{12}P_4Ru$ (1572.30) requires C, 58.06; H, 6.92; N, 7.13%.)

$[Os(N{\equiv}CNEt_2)_2\{P(OEt)_3\}_4](BPh_4)_2$ 3a and $[Os\{N{\equiv}CN(H)C(NH_2){=}NH\}_2\{P(OEt)_3\}_4](BPh_4)_2$ 3b

An equimolar amount of $CH_3OSO_2CF_3$ (0.23 mmol, 26 μL) was added to a solution of $OsH_2[P(OEt)_3]_4$ (0.23 mmol, 0.20 g) in toluene (7 cm^3) cooled to −196 °C. The reaction mixture was left to reach the room temperature, stirred for 1 h, and then cooled again to −196 °C. An equimolar amount of HOTf (0.23 mmol, 20 μL) was added and the reaction mixture brought to room temperature and stirred for 1 h. An excess of the appropriate cyanamide $N\equiv CNEt_2$ (0.70 mmol, 81 μL) or $N\equiv CNH_2$ (1.4 mmol, 59 mg) in ethanol (5 cm^3) was added and the resulting solution stirred for 3 h. The solvent was removed under reduced pressure giving an oil, which was triturated with ethanol (3 cm^3) containing an excess of $NaBPh_4$ (0.70 mmol, 0.24 g). A white solid slowly separated out from the resulting solution cooled to −25 °C, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥85%. (**3a**: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.32–6.86 (m, 40 H, Ph), 4.10, 4.02 (m, 24 H, CH_2 phos), 3.09 (q, 8 H, CH_2 NEt), 1.34, 1.31 (t, 36 H, CH_3 phos), 1.20 (t, 12 H, CH_3 NEt). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: 165–122 (m, Ph), 119.0 (t, $C\equiv N$), 63.48, 63.29 (t, CH_2 phos), 46.43 (s, CH_2 NEt), 16.45, 16.26 (t, CH_3 phos), 113.64 (s, CH_3 NEt). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: A_2B_2, δ_A 82.5, δ_B 75.7, J_{AB} = 44.0. IR (KBr)/cm^{-1}: 2275 (m) $\nu_{C\equiv N}$. Λ_M/S cm^2 mol^{-1} = 120. Found: C, 58.11; H, 7.28; N, 3.24. $C_{82}H_{120}B_2N_4O_{12}OsP_4$ (1689.60) requires C, 58.29; H, 7.16; N, 3.32%. **3b**: ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.34–6.78 (m, 40 H, Ph), 4.27, 4.17 (m, 24 H, CH_2), 4.20 (br, 8 H, NH+NH_2), 1.37, 1.34 (t, 36 H, CH_3); (CD_2Cl_2, −30 °C) 4.49 (br, 4 H, NH), 3.66 (br, 4 H, NH_2); (CD_2Cl_2, −70 °C) 4.96, 3.52 (br, 4 H, NH), 3.19 (br, 4 H, NH_2). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −70 °C) δ: A_2B_2, δ_A 88.5, δ_B 79.8, J_{AB} = 43.5. IR (KBr)/cm^{-1}: 3447, 3351, 3239 (s) ν_{NH}; 2256 (s) $\nu_{C\equiv N}$; 1633 (s) δ_{NH_2}. Λ_M/S cm^2 mol^{-1} = 117. Found: C, 55.17; H, 6.42; N, 6.63. $C_{76}H_{108}B_2N_8O_{12}OsP_4$ (1661.46) requires C, 54.94; H, 6.55; N, 6.74%.)

[RuH($N\equiv CNEt_2$){P(OEt)$_3$}$_4$]BPh_4 4a and [RuH{$N\equiv CN(H)$-$C(NH_2)=NH$}{P(OEt)$_3$}$_4$]BPh_4 4b

An equimolar amount of HOTf (0.26 mmol, 23 μL) was added to a solution of $RuH_2[P(OEt)_3]_4$ (0.26 mmol, 0.20 g) in toluene (7 cm^3) cooled to −196 °C and the reaction mixture brought to room temperature and stirred for 1 h. An excess of the appropriate cyanamide $N\equiv CNEt_2$ (0.52 mmol, 60 μL) or $N\equiv CNH_2$ (1.04 mmol, 44 mg in 3 cm^3 of ethanol) was added and the resulting solution stirred for 2 h. The solvent was removed under reduced pressure giving an oil, which was triturated with ethanol (2 cm^3) containing an excess of $NaBPh_4$ (0.52 mmol, 0.18 g). A white solid slowly separated out by cooling the resulting solution to −25 °C, which was filtered and crystallised from ethanol; yield ≥75%. (**4a**: ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.34–6.78 (m, 20 H, Ph), 4.25 (m, 24 H, CH_2 phos), 3.56 (q, 4 H, CH_2 NEt), 1.38, 1.32 (t, 36 H, CH_3 phos), 1.32 (t, 6 H, CH_3 NEt), −7.9 to −8.6 (m, 1 H, RuH). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: ABC_2, δ_A 151.9, δ_B 149.5, δ_C 140.4, J_{AB} = 63.4, J_{AC} = 46.1, J_{BC} = 42.5. IR (KBr)/cm^{-1} 2257 (s): $\nu_{C\equiv N}$. Λ_M/S cm^2 mol^{-1} = 53. Found: C, 53.54; H, 7.62; N, 2.45. $C_{53}H_{91}BN_2O_{12}P_4Ru$ (1184.07) requires C, 53.76; H, 7.75; N, 2.37%. **4b**: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.36–6.87 (m, 20 H, Ph), 4.15 (m, 4 H, NH+NH_2), 3.99 (m), 3.88 (qnt) (24 H, CH_2) 1.29, 1.26, 1.19 (t, 36 H, CH_3), −8.0 to −8.4 (m, 1 H, RuH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: ABC_2, δ_A 150.35, δ_B 147.15, δ_C 143.5, J_{AB} = 61.1, J_{AC} = 43.9, J_{BC} = 40.6. IR (KBr)/cm^{-1}: 3429, 3378, 3334 (s) ν_{NH}; 2253 (s) $\nu_{C\equiv N}$; 1631 (s) δ_{NH_2}. Λ_M/S cm^2 mol^{-1} = 59. Found: C, 51.18; H, 7.19; N, 4.67. $C_{50}H_{85}BN_4O_{12}P_4Ru$ (1170.01) requires C, 51.33; H, 7.32; N, 4.79%.)

[OsH($N\equiv CNEt_2$){P(OEt)$_3$}$_4$]BPh_4 5a and [OsH{$N\equiv CN(H)$-$C(NH_2)=NH$}{P(OEt)$_3$}$_4$]BPh_4 5b

An equimolar amount of $CH_3OSO_2CF_3$ (0.23 mmol, 26 μL) was added to a solution of $OsH_2[P(OEt)_3]_4$ (0.23 mmol, 0.20 g) in toluene (7 cm^3) and cooled to −196 °C. The reaction mixture was left to reach the room temperature, stirred for 1 h and then an excess of the appropriate cyanamide $N\equiv CNEt_2$ (0.46 mmol, 50 μL) or $N\equiv CNH_2$ (0.92 mmol, 39 mg in 3 cm^3 of ethanol) was added. The solution was stirred for 2 h and then the solvent removed under reduced pressure giving an oil, which was triturated with ethanol (2 cm^3) containing an excess of $NaBPh_4$ (0.52 mmol, 0.18 g). A white solid slowly separated out by cooling the resulting solution to −25 °C, which was filtered and crystallised from ethanol; yield ≥73%. (**5a**: ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.34–6.78 (m, 20 H, Ph), 4.10 (m), 3.97 (qnt) (24 H, CH_2 phos), 3.21 (q, 4 H, CH_2 NEt), 1.31, 1.30, 1.28 (t, 36 H, CH_3 phos), 1.25 (t, 6 H, CH_3 NEt), −8.92 to −9.48 (m, 1 H, OsH). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB_2C, δ_A 107.7, δ_B 106.2, δ_C 97.0, J_{AB} = 31.7, J_{AC} = 29.3, J_{BC} = 43.2. IR (KBr)/cm^{-1}: 2275 (s) $\nu_{C\equiv N}$; 1945 (m) ν_{OsH}. Λ_M/S cm^2 mol^{-1} = 56. Found: C, 49.82; H, 7.08; N, 2.31. $C_{53}H_{91}BN_2O_{12}OsP_4$ (1273.23) requires C, 50.00; H, 7.20; N, 2.20%. **5b**: ^1H NMR [$(CD_3)_2CO$, 25 °C] δ: 7.34–6.77 (m, 20 H, Ph), 4.23 (br, 4 H, NH + NH_2), 4.21 (m), 3.96 (qnt) (24 H, CH_2) 1.28, 1.27, 1.23 (t, 36 H, CH_3), −8.92 to −9.47 (m, 1 H, RuH); (CD_2Cl_2, −70 °C) 5.36 (br, 2 H, NH), 2.89 (br, 2 H, NH_2). $^{31}P\{^1H\}$ NMR [$(CD_3)_2CO$, 25 °C] δ: AB_2C, δ_A 109.0, δ_B 107.3, δ_C 98.4, J_{AB} = 30.4, J_{AC} = 29.5, J_{BC} = 41.9. IR (KBr)/cm^{-1}: 3423, 3390 (s) ν_{NH}; 2253 (s) $\nu_{C\equiv N}$; 1950 (m) ν_{OsH}; 1640 (s) δ_{NH_2}. Λ_M/S cm^2 mol^{-1} = 53. Found: C, 47.76; H, 6.72; N, 4.53. $C_{50}H_{85}BN_4O_{12}OsP_4$ (1259.17) requires C, 47.69; H, 6.80; N, 4.45%.)

[Fe{η^2-$NH=C(NEt_2)N(R)NH_2$}{P(OEt)$_3$}$_4$]$(BPh_4)_2$ 6a–8a (R = H 6, Me 7, Ph 8)

An excess of the appropriate hydrazine $RNHNH_2$ (0.36 mmol) was added to a solution of bis(cyanamide) complex **1a** (0.13 mmol, 0.20 g) in CH_2Cl_2 (5 cm^3) cooled to −196 °C. The reaction mixture was left to reach the room temperature and stirred for 4 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 cm^3) containing an excess of $NaBPh_4$ (0.42 mmol, 0.14 g). A white solid slowly separated out by cooling the resulting solution to −25 °C, which was filtered and crystallised from CH_2Cl_2 and ethanol; yield ≥78%. (**6a**: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.34–6.91 (m, 40 H, Ph), 5.38 (t br, 2 H, NH_2), 4.05 (m, 24 H, CH_2 phos), 3.06 (qnt, 1 H, =NH), 2.87 (q, 4 H, CH_2 NEt), 1.35, 1.33 (t, 36 H, CH_3 phos), 1.01 (t, 6 H, CH_3 NEt). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: ABC_2, δ_A 164.1, δ_B 162.5, δ_C 142.0, J_{AB} = 116.4, J_{AC} = 147.6, J_{BC} = 120.3. IR (KBr)/cm^{-1}: 3434, 3378 (s) ν_{NH}; 1619, 1603 (s) $\nu_{C=N}$, δ_{NH_2}. Λ_M/S cm^2 mol^{-1} = 128. Found: C, 61.87; H, 7.60; N, 3.72. $C_{77}H_{114}B_2FeN_4O_{12}P_4$ (1489.11) requires C, 62.11; H, 7.72; N, 3.76%. **7a**: ^1H NMR (CD_2Cl_2, 25 °C) δ: 7.34–6.89 (m, 40 H, Ph), 5.62 (t, 2 H, NH_2), 4.06 (m, 24 H, CH_2 phos), 3.86 (s br, 1 H, =NH), 3.05 (q, 4 H, CH_2 NEt), 2.89 (s, 3 H, CH_3N), 1.34, 1.33 (t, 36 H, CH_3 phos), 1.16

(t, 6 H, CH$_3$ NEt). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: ABC$_2$, δ_A 163.2, δ_B 162.1, δ_C 141.7, J_AB = 112.8, J_AC = 147.6, J_BC = 119.7. IR (KBr)/cm^{-1}: 3310, 3299 (w) ν_NH; 1616 (s) $\nu_\mathrm{C{=}N}$, $\delta_\mathrm{NH_2}$. Λ_M/S cm^2 mol^{-1} = 124. Found: C, 62.54; H, 7.67; N, 3.78. C$_{78}$H$_{116}$B$_2$FeN$_4$O$_{12}$P$_4$ (1503.14) requires C, 62.33; H, 7.78; N, 3.73%. **8a**: ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ: 7.32–6.87 (m, 45 H, Ph), 5.04 (br, 2 H, NH$_2$), 4.76 (br, 1 H, NH), 4.15, 4.03 (m, 24 H, CH$_2$ phos), 3.07 (br, 4 H, CH$_2$ NEt), 1.31 (m, 36 H, CH$_3$ phos), 1.20 (br, 6 H, CH$_3$ NEt). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: ABC$_2$, δ_A 148.7, δ_B 143.4, δ_C 134.0, J_AB = 140.0, J_AC = 126.5, J_BC = 142.0. IR (KBr)/cm^{-1}: 3429, 3387 (m) ν_NH. Λ_M/S cm^2 mol^{-1} = 122. Found: C, 63.46; H, 7.58; N, 3.45. C$_{83}$H$_{118}$B$_2$FeN$_4$O$_{12}$P$_4$ (1565.21) requires C, 63.69; H, 7.60; N, 3.58%.)

[Fe{η^2-NH=C[N=C(NH$_2$)$_2$]NHNH$_2$}{P(OEt)$_3$}$_4$](BPh$_4$)$_2$ 6b and [Fe{η^2-NH=C[N=C(NH$_2$)$_2$]N(Me)NH$_2$}{P(OEt)$_3$}$_4$](BPh$_4$)$_2$ 7b

The complexes were prepared like the related **6a**, **7a** by reacting bis(cyanoguanidine) complex **1b** with the appropriate hydrazine RNHNH$_2$ for 5 h; yield ≥60%. (**6b**: ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ: 7.35–6.92 (m, 40 H, Ph), 5.32 (t, 2 H, NH$_2$N), 4.00 (m, 24 H, CH$_2$), 3.84 (br, 4 H, NH$_2$C), 2.23 (br, 1 H, NH), 1.31 (t br, 36 H, CH$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: ABC$_2$, δ_A 162.0, δ_B 159.4, δ_C 143.3, J_AB = 114.3, J_AC = 121.3, J_BC = 134.9. IR (KBr)/cm^{-1}: 3434, 3400, 3366 (s), 3320 (w) ν_NH; 1626 (s) $\nu_\mathrm{C{=}N}$, $\delta_\mathrm{NH_2}$. Λ_M/S cm^2 mol^{-1} = 120. Found: C, 60.12; H, 7.51; N, 5.58. C$_{74}$H$_{108}$B$_2$FeN$_6$O$_{12}$P$_4$ (1475.04) requires C, 60.26; H, 7.38; N, 5.70%. **7b**: ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ: 7.36–6.91 (m, 40 H, Ph), 5.47 (t, 2 H, NH$_2$N), 4.03 (m, 24 H, CH$_2$), 3.87 (br, 4 H, NH$_2$C), 3.42 (br, 1 H, NH), 3.01 (s, 3 H, CH$_3$N), 1.30 (t, 36 H, CH$_3$ phos). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: ABC$_2$, δ_A 164.5, δ_B 162.7, δ_C 142.7, J_AB = 114.0, J_AC = 146.5, J_BC = 115.6. IR (KBr)/cm^{-1}: 3412, 3378, 3345 (s), 3340 (w) ν_NH; 1627, 1614 (s) $\nu_\mathrm{C{=}N}$, $\delta_\mathrm{NH_2}$. Λ_M/S cm^2 mol^{-1} = 128. Found: C, 60.35; H, 7.37; N, 5.61. C$_{75}$H$_{110}$B$_2$FeN$_6$O$_{12}$P$_4$ (1489.07) requires C, 60.49; H, 7.45; N, 5.64%.)

[Ru{η^2-NH=C(NEt$_2$)NHNH$_2$}{P(OEt)$_3$}$_4$](BPh$_4$)$_2$ 9a and [Ru{η^2-NH=C(NEt$_2$)N(Me)NH$_2$}{P(OEt)$_3$}$_4$](BPh$_4$)$_2$ 10a

An excess of the appropriate hydrazine RNHNH$_2$ (0.30 mmol) was added to a solution of bis(cyanamide) complex **2a** (0.12 mmol, 0.20 g) in 1,2-dichloroethane (7 cm^3) and the reaction mixture refluxed for 30 min. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 cm^3) containing an excess of NaBPh$_4$ (0.36 mmol, 0.12 g). By cooling the resulting solution to −25 °C, a white solid slowly separated out which was filtered and crystallised from CH$_2$Cl$_2$ and ethanol; yield ≥65%. (**9a**: ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ: 7.33–6.87 (m, 40 H, Ph), 6.14 (br, 1 H, NH), 5.54 (q br, 2 H, NH$_2$), 4.04 (m, 24 H, CH$_2$ phos), 3.45 (m, 1 H, NH), 2.92 (q, 4 H, CH$_2$ NEt), 1.34, 1.33, 1.31 (t, 36 H, CH$_3$ phos), 1.05 (t, 6 H, CH$_3$ NEt). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: ABC$_2$, δ_A 135.1, δ_B 133.7, δ_C 119.3, J_AB = 72.7, J_AC = 63.4, J_BC = 57.6. IR (KBr)/cm^{-1}: 3429, 3311 (m) ν_NH; 1617, 1598 (s) $\nu_\mathrm{C{=}N}$, $\delta_\mathrm{NH_2}$. Λ_M/S cm^2 mol^{-1} = 116. Found: C, 60.43; H, 7.37; N, 3.58. C$_{77}$H$_{114}$B$_2$N$_4$O$_{12}$P$_4$Ru (1534.34) requires C, 60.28; H, 7.49; N, 3.65%. **10a**: ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ: 7.34–6.86 (m, 40 H, Ph), 5.70 (q br, 2 H, NH$_2$), 4.33 (br, 1 H, NH), 4.05 (m, 24 H, CH$_2$ phos), 3.04 (q, 4 H, CH$_2$ NEt), 2.87 (s, 3 H, CH$_3$N), 1.34, 1.33, 1.31 (t, 36 H, CH$_3$ phos), 1.15 (t, 6 H, CH$_3$ NEt). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: ABC$_2$, δ_A 134.3, δ_B 133.1, δ_C 118.7, J_AB = 72.4, J_AC = 63.5, J_BC = 57.3. IR (KBr)/cm^{-1}: 3429 (m), 3395, 3295 (w) ν_NH; 1613 (s) $\nu_\mathrm{C{=}N}$, $\delta_\mathrm{NH_2}$. Λ_M/S cm^2 mol^{-1} = 121. Found: C, 60.34; H, 7.60; N, 3.50. C$_{78}$H$_{116}$B$_2$N$_4$O$_{12}$P$_4$Ru (1548.36) requires C, 60.50; H, 7.55; N, 3.62%.)

[Ru{η^2-NH=C[N=C(NH$_2$)$_2$]N(Me)NH$_2$}{P(OEt)$_3$}$_4$](BPh$_4$)$_2$ 10b

This compound was prepared exactly like the related **10a** starting from bis(cyanoguanidine) complex **2b** and using methylhydrazine as a reagent; yield ≥65%. (^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ: 7.35–6.90 (m, 40 H, Ph), 5.62 (q, 2 H, NH$_2$N), 4.02 (m, 24 H, CH$_2$), 3.78 (br, 4 H, NH$_2$C), 3.05 (s, 3 H, CH$_3$N), 1.32, 1.30 (t, 36 H, CH$_3$ phos). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: 165–122 (m, Ph), 164.04 (s, C=NH), 63.35, 60.0 (m, CH$_2$), 40.58 (s, CH$_3$N), 16.34 (m, CH$_3$ phos). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: ABC$_2$, δ_A 135.6, δ_B 133.2, δ_C 119.2, J_AB = 70.6, J_AC = 63.3, J_BC = 57.1. IR (KBr)/cm^{-1}: 3445, 3357 (s) ν_NH; 1635, 1617 (s) $\nu_\mathrm{C{=}N}$, $\delta_\mathrm{NH_2}$. Λ_M/S cm^2 mol^{-1} = 125. Found: C, 58.58; H, 7.35; N, 5.37. C$_{75}$H$_{110}$B$_2$N$_6$O$_{12}$P$_4$Ru (1534.30) requires C, 58.71; H, 7.23; N, 5.48%.)

[Os{η^2-NH=C(NEt$_2$)NHNH$_2$}{P(OEt)$_3$}$_4$](BPh$_4$)$_2$ 11a and [Os{η^2-NH=C(NEt$_2$)N(Me)NH$_2$}{P(OEt)$_3$}$_4$](BPh$_4$)$_2$ 12a

An excess of the appropriate hydrazine RNHNH$_2$ (0.36 mmol) was added to a solution of bis(cyanamide) complex **3a** (0.12 mmol, 0.20 g) in 1,2-dichloroethane (7 cm^3) and the reaction mixture refluxed for 1 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 cm^3) containing an excess of NaBPh$_4$ (0.36 mmol, 0.12 g). By cooling the resulting solution to −25 °C, a white solid slowly separated out which was filtered and crystallised from CH$_2$Cl$_2$ and ethanol; yield ≥70%. (**11a**: ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ: 7.32–6.89 (m, 40 H, Ph), 5.84 (m br, 2 H, NH$_2$), 5.58 (m br, 1 H, NH), 4.03 (m, 24 H, CH$_2$ phos), 3.85 (m, 1 H, NH), 2.79 (q, 4 H, CH$_2$ NEt), 1.33, 1.32, 1.30 (t, 36 H, CH$_3$ phos), 0.98 (t, 6 H, CH$_3$ NEt). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: 165–122 (m, Ph), 159.37 (s, C=NH), 63.46 (m, CH$_2$ phos), 46.44 (s, CH$_2$ NEt), 16.45, 16.31, 16.26 (t, CH$_3$ phos), 13.65 (s, CH$_3$ NEt). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: ABC$_2$, δ_A 86.6, δ_B 83.3, δ_C 83.0, J_AB = 40.1, J_AC = 42.0, J_BC = 38.9. IR (KBr)/cm^{-1}: 3435 (m), 3306, 3260 (w) ν_NH; 1628, 1605 (s) $\nu_\mathrm{C{=}N}$, $\delta_\mathrm{NH_2}$. Λ_M/S cm^2 mol^{-1} = 122. Found: C, 56.76; H, 7.17; N, 3.36. C$_{77}$H$_{114}$B$_2$N$_4$O$_{12}$OsP$_4$ (1623.50) requires C, 56.96; H, 7.08; N, 3.45%. **12a**: ^{1}H NMR (CD$_2$Cl$_2$, 25 °C) δ: 7.33–6.88 (m, 40 H, Ph), 6.20 (br, 2 H, NH$_2$), 5.08 (br, 1 H, NH), 4.03 (m, 24 H, CH$_2$ phos), 3.05 (m, 4 H, CH$_2$ NEt), 2.78 (s, 3 H, CH$_3$N), 1.33, 1.31, 1.29 (t, 36 H, CH$_3$ phos), 1.14 (t, 6 H, CH$_3$ NEt). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C) δ: ABC$_2$, δ_A 85.9, δ_B 82.6, δ_C 82.4, J_AB = 41.8, J_AC = 41.1, J_BC = 41.0. IR (KBr)/cm^{-1}: 3434 (m), 3283 (w) ν_NH; 1614 (s) $\nu_\mathrm{C{=}N}$, $\delta_\mathrm{NH_2}$. Λ_M/S cm^2 mol^{-1} = 118. Found: C, 57.00; H, 7.22; N, 3.49. C$_{78}$H$_{116}$B$_2$N$_4$O$_{12}$OsP$_4$ (1637.52) requires C, 57.21; H, 7.14; N, 3.42%.)

$[Os\{\eta^2\text{-}NH{=}C[N{=}C(NH_2)_2]N(Me)NH_2\}\{P(OEt)_3\}_4](BPh_4)_2$ 12b

This compound was prepared exactly like the related **11a** starting from bis(cyanoguanidine) complex **3b** and using methylhydrazine as a reagent; yield ≥65%. (^1H NMR (CD_2Cl_2, 25 °C) δ: 7.36–6.91 (m, 40 H, Ph), 6.17 (q, 2 H, NH_2N), 4.39 (s, 1 H, NH), 4.04 (m, 24 H, CH_2), 3.78 (s br, 4 H, NH_2C), 3.03 (s, 3 H, CH_3N), 1.30, 1.29 (t, 36 H, CH_3 phos). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 25 °C) δ: ABC_2, δ_A 87.1, δ_B 83.6, δ_C 82.4, J_{AB} = 40.7, J_{AC} = 40.0, J_{BC} = 44.1. IR (KBr)/cm^{-1}: 3440, 3402, 3355 (s) ν_{NH}; 1628, 1620 (s) $\nu_{C=N}$, δ_{NH_2}. Λ_M/S cm^2 mol^{-1} = 123. Found: C, 55.33; H, 6.75; N, 5.07. $C_{75}H_{110}B_2N_6O_{12}OsP_4$ (1623.46) requires C, 55.49; H, 6.83; N, 5.18%.)

X-ray crystallography

Crystallographic data were collected on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å), and were corrected for Lorentz and polarisation effects. The software SMART[21] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT[22] for integration of intensity of reflections and scaling, and SADABS[23] for empirical absorption correction.

The crystallographic treatment was performed with the Oscail program.[24] The structure was solved by direct methods and refined by full-matrix least-squares based on F^2.[25] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters. Unfortunately, the quality of the best crystal obtained is limited, and values of 9.6% for R(int) and 14.6% for $R(\sigma)$ were obtained. However, there is no doubt about the correct assignment of the atoms. Details of crystal data and structural refinement are given in Table 1, selected bond lengths and angles are shown in Table 2. CCDC 985290 contains the supplementary crystallographic data for this paper.

Table 1 Crystal data and structure refinement

Identification code	**12b**
Empirical formula	$C_{75}H_{110}B_2N_6O_{12}P_4Os$
Formula weight	1623.39
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 17.0333(13) Å
	b = 20.4889(16) Å
	c = 24.4972(19) Å
	α = 90°
	β = 90°
	γ = 90°
Volume	8549.4(11) $Å^3$
Z	4
Density (calculated)	1.261 Mg m^{-3}
Absorption coefficient	1.623 mm^{-1}
$F(000)$	3376
Crystal size	0.36 × 0.15 × 0.14 mm
Θ Range for data collection	1.30 to 28.04°
Index ranges	$-22 \le h \le 21$
	$-27 \le k \le 27$
	$-31 \le l \le 18$
Reflections collected	57 250
Independent reflections	20361, [R(int) = 0.0964]
Reflections observed (>2σ)	9855
Data completeness	0.994
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6536
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	20 361/0/914
Goodness-of-fit on F^2	0.954
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0509, R_2 = 0.0870
R indices (all data)	R_1 = 0.1590, wR_2 = 0.1185
Absolute structure parameter	−0.016(7)
Largest diff. peak and hole	1.288 and −1.396 (e $Å^{-3}$)

Table 2 Selected bond lengths [Å] and angles [°] for **12b**

Os–N(3)	2.113(5)	Os–N(1)	2.162(5)
Os–P(1)	2.249(2)	Os–P(3)	2.2710(18)
Os–P(2)	2.327(2)	Os–P(4)	2.337(2)
N(1)–N(2)	1.428(7)	N(2)–C(1)	1.371(9)
N(2)–C(2)	1.436(8)	C(1)–N(3)	1.300(8)
C(1)–N(4)	1.346(8)	N(4)–C(4)	1.291(11)
C(4)–N(5)	1.357(12)	C(4)–N(6)	1.364(12)
N(3)–Os–N(1)	75.7(2)	N(3)–Os–P(1)	94.07(16)
N(1)–Os–P(3)	91.28(14)	P(1)–Os–P(3)	98.90(8)
N(3)–Os–P(2)	85.57(15)	N(1)–Os–P(2)	87.72(16)
P(1)–Os–P(2)	91.68(8)	P(3)–Os–P(2)	95.02(7)
N(3)–Os–P(4)	85.84(15)	N(1)–Os–P(4)	87.64(16)
P(1)–Os–P(4)	91.53(8)	P(3)–Os–P(4)	92.77(8)
N(1)–Os–P(1)	169.81(15)	N(3)–Os–P(3)	166.99(16)
P(2)–Os–P(4)	171.02(7)	N(2)–N(1)–Os	112.0(4)
C(1)–N(2)–N(1)	116.2(5)	C(1)–N(2)–C(2)	124.7(6)
N(1)–N(2)–C(2)	119.0(6)	N(3)–C(1)–N(4)	126.9(7)
N(3)–C(1)–N(2)	118.5(6)	N(4)–C(1)–N(2)	114.6(7)
C(1)–N(3)–Os	117.5(5)	C(4)–N(4)–C(1)	123.0(9)
N(4)–C(4)–N(5)	123.9(9)	N(4)–C(4)–N(6)	118.4(11)
N(5)–C(4)–N(6)	117.6(11)		

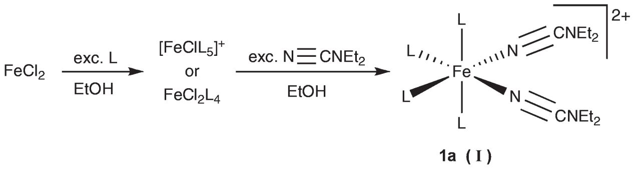
Results and discussion

Preparation of bis(cyanamide) complexes of Fe

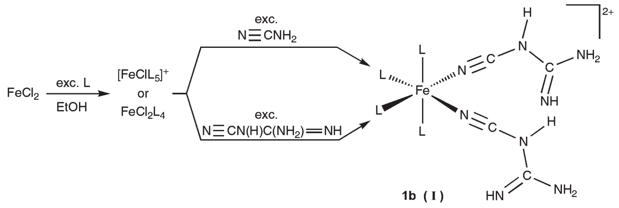
Iron(II) bis(diethylcyanamide) complex $[Fe(N{\equiv}CNEt_2)_2L_4](BPh_4)_2$ **1a** [L = $P(OEt)_3$] was prepared by reacting anhydrous iron(II) chloride first with an excess of phosphite and then with an excess of cyanamide, as shown in Scheme 1.

The reaction of iron(II) chloride with phosphites was reported[26] to give a mixture of complexes, in which $[FeClL_5]^+$ and $FeCl_2L_4$ were predominant. The substitution of Cl^- and/or L by $N{\equiv}CNEt_2$ in these intermediates afforded the bis(diethylcyanamide) cation **1a**, which was isolated as the BPh_4 salt and characterised.

Cyanamide $N{\equiv}CNH_2$ also reacted with phosphite-containing iron(II) complexes, but yielded the bis(cyanoguanidine) derivative $[Fe\{N{\equiv}CN(H)C(NH_2){=}NH\}_2L_4](BPh_4)_2$ **1b** (Scheme 2). The formation of this complex is not very surprising, owing to the known ease of dimerizing of $N{\equiv}CNH_2$, affording cyanoguanidine, which acts as a ligand in the complex. Dimerisation[16] may be promoted by the coordination of one cyanamide $[Fe]{-}N{\equiv}CNH_2$ followed by nucleophilic attack on its $C{\equiv}N$ carbon atom of a second cyanamide affording, after tautomerisation, a N-bonded imine-cyanoguanidine complex $[Fe]{-}N(H){=}C(NH_2)N(H)C{\equiv}N$. The linkage isomerisation of



Scheme 1 L = $P(OEt)_3$.



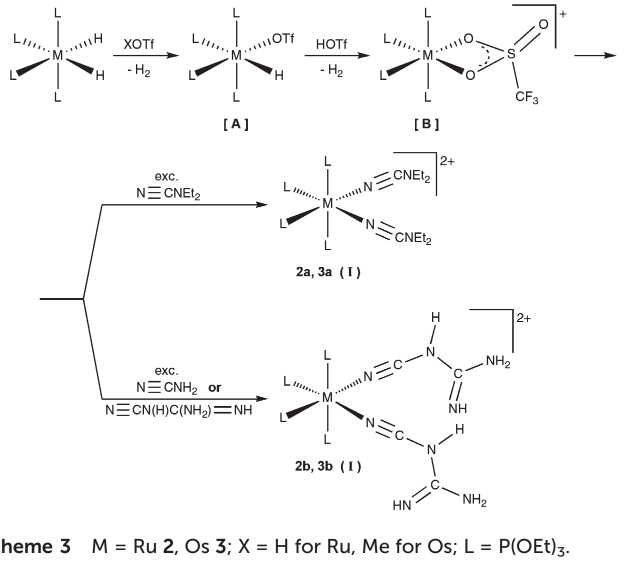
Scheme 2 L = $P(OEt)_3$.

this ligand gave the N-nitrile-bonded derivative. The same complex **1b** was in fact prepared by reacting iron(II) chloride first with phosphite and then with an excess of cyanoguanidine, as shown in Scheme 2.

Preparation of bis(cyanamide) complexes of Ru and Os

The easy synthesis of iron complexes **1a** and **1b** prompted us to extend the study to ruthenium and osmium, but a different route had to be followed for them, involving dihydrides MH_2L_4 as precursors.

Sequential treatment of RuH_2L_4 first with one equivalent of triflic acid, then with another, and lastly with an excess of the appropriate cyanamide, afforded bis(diethylcyanamide) $[Ru(N{\equiv}CNEt_2)_2L_4](BPh_4)_2$ **2a** and bis(cyanoguanidine) $[Ru\{N{\equiv}CN(H)C(NH_2){=}NH\}_2L_4](BPh_4)_2$ **2b** derivatives, which were isolated in good yields and characterised (Scheme 3). The reaction of RuH_2L_4 with HOTf proceeded[15c,27] with the evolution of H_2 and formation of $RuH(\kappa^1\text{-OTf})L_4$ [**A**], which further reacted with HOTf, yielding the cation $[Ru(\kappa^2\text{-}O_2SOCF_3)L_4]^+$ [**B**]. Substitution of the $\kappa^2\text{-}O_2SOCF_3$ ligand with the appropriate N≡CNR1R2 in [**B**] afforded bis(diethylcyanamide) **2a** and bis(cyanoguanidine) **2b** derivatives.



Scheme 3 M = Ru **2**, Os **3**; X = H for Ru, Me for Os; L = $P(OEt)_3$.

A slight modification of this method was necessary to prepare osmium cyanamide complexes, involving treatment of OsH_2L_4 first with methyl triflate, then with triflic acid and lastly with an excess of the appropriate cyanamide, affording bis(diethylcyanamide) $[Os(N{\equiv}CNEt_2)_2L_4](BPh_4)_2$ **3a** and bis(cyanoguanidine) $[Os\{N{\equiv}CN(H)C(NH_2){=}NH\}_2L_4](BPh_4)_2$ **3b** derivatives (Scheme 3). Methyl triflate MeOTf reacted with OsH_2L_4, with the evolution of methane and formation[15a,28] of $OsH(\kappa^1\text{-OTf})L_4$ [**A**], which further reacted with HOTf, yielding the cation $[Os(\kappa^2\text{-}O_2SOCF_3)L_4]^+$ [**B**]. Methyl triflate was used instead of triflic acid in the case of osmium, due to the stability of the $\eta^2\text{-}H_2$ intermediate $[OsH(\eta^2\text{-}H_2)L_4]^+$,[27,28] which prevents formation of the key-intermediate $[Os(\kappa^2\text{-}O_2SOCF_3)L_4]^+$, yielding the final derivatives **3a** and **3b**.

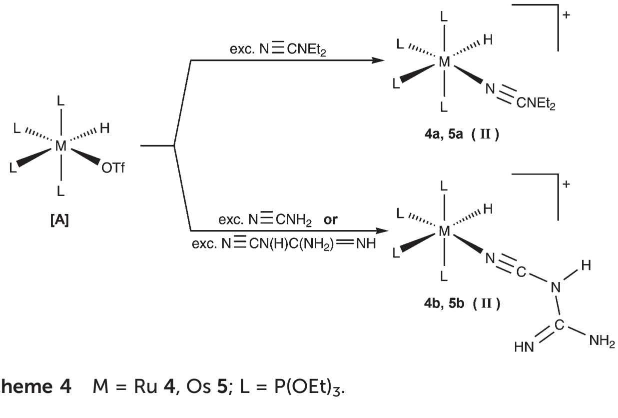
As observed for iron, the reaction with cyanamide $N{\equiv}CNH_2$ of triflate intermediates of both Ru and Os afforded cyanoguanidine derivatives **2b** and **3b** through dimerisation of the $N{\equiv}CNH_2$ species. The same bis(cynoguanidine) complexes were also obtained with $N{\equiv}CN(H)C(NH_2){=}NH$ as a reagent.

Bis(cyanamide) and bis(cyanoguanidine) complexes of transition metals are very rare and have only been described for nickel and copper triads.[1,6f] The use of tetrakis(phosphite) fragments $[M\{P(OEt)_3\}_4]^{2+}$ allowed the synthesis of the first examples of bis(cyanamide) derivatives of the iron triad.

Dihydride complexes MH_2L_4 were used to prepare bis(cyanamide) complexes **2** and **3**, and prompted us also to prepare mono-cyanamide $[MH(N{\equiv}CNEt_2)L_4]BPh_4$ **4a**, **5a** and mono-cyanoguanidine derivatives $[MH\{N{\equiv}CN(H)C(NH_2){=}NH\}_2L_4]BPh_4$ **4b**, **5b** by reacting hydride-triflate species $MH(\kappa^1\text{-OTf})L_4$ [**A**] with an excess of the appropriate cyanamide, as shown in Scheme 4. The reaction proceeded quickly, with substitution of the triflate ligand and formation of cyanamide cations **4** and **5**, which were isolated as BPh_4 salts in good yields.

Characterisation of cyanamide derivatives

Good analytical data were obtained for both mono-$[MH(N{\equiv}CNR1R2)L_4]BPh_4$ **4**, **5** and bis(cyanamide)/(cyano-



Scheme 4 M = Ru **4**, Os **5**; L = $P(OEt)_3$.

guanidine) complexes $[M(N{\equiv}CNR1R2)_2L_4](BPh_4)_2$ **1–3**, which were all isolated as white or yellow solids stable in air and in solution of polar organic solvents, in which they behave as 1 : 1 (**4**, **5**) or 2 : 1 (**1–3**) electrolytes.[29] Infrared and NMR data support the proposed formulations for the complexes, which were also indirectly confirmed by X-ray crystal structure determinations of complex **12b** (see below).

The IR spectra of bis(diethylcyanamide) complexes $[M(N{\equiv}CNEt_2)_2L_4](BPh_4)_2$ **1a–3a** showed one medium-intensity band at 2275–2264 cm^{-1}, attributed to the ν_{CN} of the cyanamide ligands. The presence of only one band indicates that the two $N{\equiv}CNEt_2$ ligands are in a mutually *trans* position. However, this hypothesis contrasted with ^{31}P NMR spectra which, in the temperature range +20 to −80 °C, were symmetric A_2B_2 multiplets, indicating the presence of two-by-two magnetically equivalent phosphine ligands. On this basis, *cis* geometry **I** can be proposed for bis(diethylcyanamide) complexes **1a**, **2a** and **3a**. The expected two absorptions in the IR spectra for the ν_{CN} of the *cis*-cyanamide may have such close values that the instrument detected only one signal, with a slightly broad band.

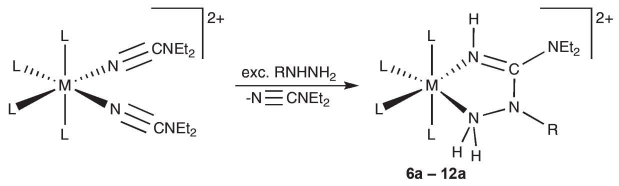
The IR spectra of bis(cyanoguanidine) complexes $[M\{N{\equiv}CN(H)C(NH_2){=}NH\}_2L_4](BPh_4)_2$ **1b–3b** showed either three or four bands of medium to weak intensity in the region 3447–3233 cm^{-1}, attributed to the ν_{NH} of the cyanoguanidine ligands. One medium-intensity band also appeared at 2256–2246 cm^{-1} and was attributed to the ν_{CN} of the same ligands. The presence of only one band indicated that the cyanoguanidine ligands were present in the amine form. A strong absorption at 1633–1630 cm^{-1} was also seen in the IR spectra, due to the δ_{NH_2} of the nitrogenous ligand. Also in this case, the IR instrument probably did not resolve the ν_{CN} absorptions, showing only one slightly broad band at 2256–2246 cm^{-1} for the two *cis*-cyanamide ligands. At room temperature, the ^1H NMR spectra of cyanoguanidine complexes **1b**, **2b** and **3b** showed the characteristic signals of phosphites and BPh_4^- anions, and a broad signal between 4.16 and 4.24 ppm attributable to either NH_2 or NH protons of the cyanoguanidine. However, lowering the sample temperatures changed the profiles of the spectra and, at −70 °C, three broad signals appeared between 5.14 and 3.19 ppm, with an intensity ratio of about 1 : 1 : 2, which were attributed to the NH and NH_2 protons of the cyanoguanidine ligands. In the ^{13}C NMR spectrum of **2b**, a singlet at 162.2 ppm was attributed to the amine $-C(NH_2){=}NH$ carbon resonance and a triplet at 121.9 ppm to the nitrile one, fitting the proposed formulation for the complexes. In the temperature range +20 to −80 °C, the ^{31}P NMR spectra of complexes **1b**, **2b** and **3b** were A_2B_2 multiplets, indicating the mutually *cis* position of the two cyanoguanidine ligands (geometry **I**, Scheme 2).

The IR spectra of hydride–diethylcyanamide complexes $[MH(N{\equiv}CNEt_2)L_4]BPh_4$ **4a**, **5a** showed the ν_{CN} band at 2275–2264 cm^{-1}, whereas those of hydride-cyanoguanidine derivatives $[MH\{N{\equiv}CN(H)C(NH_2){=}NH\}L_4]BPh_4$ **4b**, **5b** showed ν_{NH} absorptions between 3429 and 3334 cm^{-1} and ν_{CN} at 2253 cm^{-1}. The ^1H NMR spectra confirmed the presence of the nitrogenous ligands, showing the signals of ethyl substituents for $N{\equiv}CNEt_2$ compounds **4a** and **5a**, whereas three broad signals at 5.36–2.89 ppm, attributable to the NH and NH_2 of cyanoguanidine, were observed in the low-temperature spectrum (−70 °C) of **5b**. A low-frequency multiplet between −7.90 and −9.48 ppm, due to hydride resonance, was also observed in the spectra of complexes **4** and **5**. In the temperature range +20 to −80 °C, the ^{31}P NMR spectra of complexes were either ABC_2 or AB_2C multiplets, indicating that the hydride and cyanamide or cyanoguanidine ligands were in a mutually *cis* position, as in geometry **II** (Scheme 4).

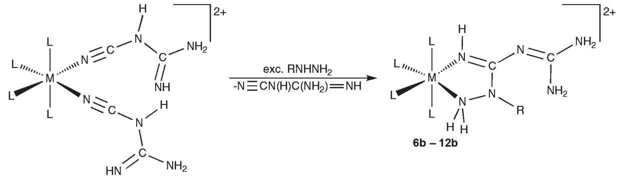
Reactivity with hydrazine

Bis(diethylcyanamide) $[M(N{\equiv}CNEt_2)_2L_4]^{2+}$ **1a–3a** and bis(cyanoguanidine) complexes $[M\{N{\equiv}CN(H)C(NH_2){=}NH\}_2L_4]^{2+}$ **1b–3b** reacted with hydrazines $RNHNH_2$ to give white solids, characterised as the hydrazinecarboximidamide complexes $[M\{\eta^2\text{-}N(H){=}C(NEt_2)N(R)NH_2\}L_4](BPh_4)_2$ **6a–12a** and $[M\{\eta^2\text{-}N(H){=}C[N{=}C(NH_2)_2]N(R)NH_2\}L_4](BPh_4)_2$ **6b–12b** (Schemes 5 and 6).

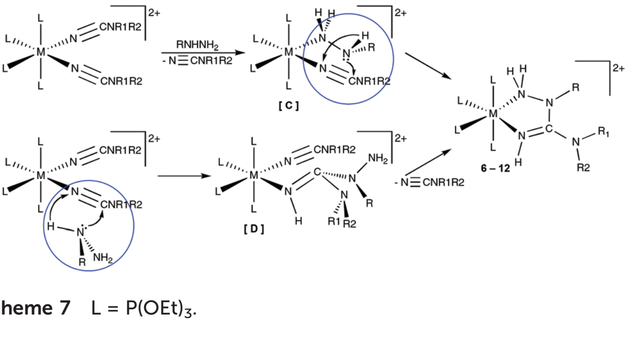
The formation of azametallocycle[30] compounds **6–12** may be explained (Scheme 7) through substitution of one cyanamide by $RNHNH_2$ giving the $[M(N{\equiv}CNR1R2)(RNHNH_2)L_4]^{2+}$ intermediate [**C**], in which one end of the hydrazine can attack



Scheme 5 M = Fe **6–8**, Ru **9**, **10**, Os **11**, **12**; R = H **6**, **9**, **11**, Me **7**, **10**, **12**, Ph **8**; L = $P(OEt)_3$.



Scheme 6 M = Fe **6**, **7**, Ru **9**, **10**, Os **11**, **12**; R = H **6**, **9**, **11**, Me **7**, **10**, **12**; L = $P(OEt)_3$.



Scheme 7 L = $P(OEt)_3$.

the carbon atom of the coordinate cyanamide giving the five-membered azametallocycle. Direct nucleophilic attack at the CN group of one cyanamide or cyanoguanidine, yielding η^1-hydrazinecarboximidamide [**D**] in Scheme 7, should be ruled out insofar as the bifunctional nucleophile $RNHNH_2$ cannot attack the C atom by more sterically encumbered end.

Nucleophilic attack on coordinate dialkyl cyanamide or cyanoguanidine has been reported with amine, imine or alcohol groups,[6f,g,13,31] but none with hydrazine. The coordination of two N≡CNR1R2 groups to the tetrakis(phosphite) fragment $[M\{P(OEt)_3\}_4]^{2+}$ allowed an easy reaction with hydrazine, yielding chelate triazametallocycle complexes **6–12**. However, crucial for the formation of the hydrazinecarboximidamide group through nucleophilic attack of $RNHNH_2$ on the nitrile carbon atom of N≡CNR1R2 was the presence of a labile ligand such as cyanamide itself, the easy substitution of which yielded the chelate azametallocycle.

The reaction of hydrazines on coordinate nitriles giving amidrazones was reported by us[15] and, long ago, by Shaw *et al.*,[32] who found the facile oxidation of such species. In our case, the chelation of the azo ligand prevents its oxidation in the complexes.

The related hydrazido-cyanamide complexes $[MH(N{\equiv}CNR1R2)L_4]BPh_4$ **4**, **5** did not react with hydrazine under all conditions, probably because of the absence of a labile ligand, which prevented the formation of the chelate hydrazinecarboximidamide group.

The new azametallocycle complexes **6–12** were isolated as white (Ru, Os) or pale-yellow (Fe) solids, very stable in air and in solution of polar organic solvents, in which they behave as 2 : 1 electrolytes.[29] Their formulation is supported by analytical and spectroscopic (IR and NMR) data and by X-ray crystal structure determination of complex $[Os\{\eta^2\text{-}NH{=}C[N{=}C(NH_2)_2]N(CH_3)NH_2\}\{P(OEt)_3\}_4](BPh_4)_2$ **12b**, the ORTEP of which is shown in Fig. 1.

The asymmetric unit in **12b** contains two tetraphenylborate anions and a bivalent cationic osmium complex. The osmium atom in the cationic complex is coordinated by four triethylphosphite ligands and a *N*,*N*′-bidentate *N*-(diaminomethylene)-1-methyl-hydrazinecarboximidamide ligand with a chelating angle of 75.7(2)°. The overall geometry may be described as a slightly distorted octahedron. Another source of distortion in the octahedron, apart from the bite angle, is the slight bend of the mutually *trans* phosphorus atoms toward the *N*,*N*′-bidentate ligand, no doubt due to the steric requirements of phosphites. Both effects give *trans* angles from 166.99(16) to 171.02(7)°, more than 10° deviated from regularity on average. The four phosphites are in two groups, those mutually *trans*, with Os–P bond lengths of 2.337(2) and 2.327(2) Å, and those *trans* to the nitrogen atoms, with slightly shorter Os–P bond lengths, 2.249(2) and 2.2710(18) Å.[15a] The octahedron may be described as having the nitrogen atoms in a very regular equatorial plane, the dihedral angle between the RuPP and RuNN planes being only 2.6(2)°. The Os–N bond lengths of 2.113(5) and 2.162(5) Å are only slightly shorter than those found in other tetraphosphite–osmium complexes with OsP_4N_2 cores.[14b,15a] The 1-methyl-hydrazinecarboximidamide moiety in the nitrogenated ligand is essentially planar, with rms deviation of only 0.0258 Å, so that both N(2) and C(1) are sp^2 hybridised. The sums of the angles around these atoms are in fact 359.9 and 360.1° respectively. The *N*-(diaminomethylene) group is out-of-plane and twisted, forming a dihedral angle of 46.9(4)° with the first plane. The N(4)–C(4) bond distance of 1.291(11) Å clearly corresponds to a double bond. All the other C–C and C–N bond lengths in the carboximidamide, between 1.300(8) and 1.371(9) Å, are shorter than values expected for single bonds, and are indicative of some kind of delocalisation.

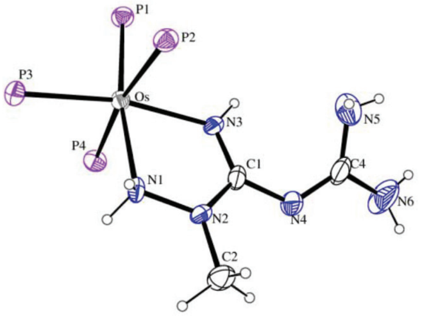


Fig. 1 ORTEP[33] view of the cation of **12b**, drawn at 30% probability level. Ethoxy groups on all the phosphites were not drawn for clarity.

The IR spectra of *N*,*N*-diethyl-1-hydrazinecarboximidamide complexes $[M\{\eta^2\text{-}NH{=}C(NEt_2)N(R)NH_2\}L_4](BPh_4)_2$ **6a–12a** show the ν_{NH} of the NH and NH_2 groups as medium or weak bands between 3435 and 3260 cm^{-1}, whereas δ_{NH_2} and/or $\nu_{C{=}N}$ appear as strong absorptions at 1627–1598 cm^{-1}. As well as the signals of phosphites and BPh_4^- anion, the ^1H NMR spectra show a quartet and a triplet of ethyl substituents NEt_2 and two broad signals between 6.14 and 3.06 ppm, of intensity ratio 2 : 1, attributed to the amine NH_2 and imine ═NH protons of the azametallocycle ligand. The spectra also display the signals of the substituent R of the hydrazine nitrogen atom, matching the presence of the azo ligand. The ^{31}C NMR spectra of **11a** show the expected signals of the ligands; in particular, a singlet at 159.37 ppm was attributed to the imine HN═C carbon resonance of the carboximidamide ligand, whereas the ^{31}P spectra are ABC_2 multiplets, matching the proposed formulation.

The IR spectra of *N*-carbamimidoyl-1-hydrazinecarboximidamide derivatives $[M\{\eta^2\text{-}NH{=}C[N{=}C(NH_2)_2]NRNH_2\}L_4](BPh_4)_2$ **6b**, **7b**, **10b**, **12b** showed several bands in the 3445–3320 cm^{-1} region, attributed to the ν_{NH} of the NH and NH_2 groups of the azometallacycle ligand. The δ_{NH_2} is observed as a strong absorption at 1635–1617 cm^{-1}. However, the presence of this ligand was confirmed by ^1H NMR spectra, which showed three broad signals between 6.17 and 3.42 ppm, of intensity ratio 2 : 4 : 1, attributed to the NH_2, $[N{=}C(NH_2)_2]$ and ═NH groups. The spectra also show the signals of the substituent to the N(R) nitrogen atoms, either as singlets at

3.03–3.05 ppm for R = Me (**7b**, **10b**, **12b**) or as a hump at 2.23 ppm for R = H (**6b**). In the ^{13}C NMR spectrum of **10b**, the resonance of the imine N═C carbon atoms appears at 164.04 ppm and that of the methyl substituent $N(CH_3)$ at 40.58 ppm, fitting the proposed formulation. In the temperature range +20 to −80 °C, the ^{31}P NMR spectra of complexes **6b**, **7b**, **10b**, **12b** appear as ABC_2 multiplets, indicating that a geometry like that found in the solid state occurs in solution.

Conclusions

This paper reports the preparation of the first bis(dialkylcyanamide) $[M(N{\equiv}CNEt_2)_2L_4](BPh_4)_2$ and bis(cyanoguanidine) $[M\{N{\equiv}CN(H)C(NH_2){=}NH\}_2L_4](BPh_4)_2$ complexes of the iron triad. Among the properties shown by these complexes, is the reaction with hydrazine, which proceeds with nucleophilic attack on the cyanamide carbon atom, affording chelate η^2-hydrazinecarboximidamide derivatives $[M\{\eta^2\text{-}N(H){=}C(NEt_2)\text{-}N(R)NH_2\}L_4](BPh_4)_2$.

Acknowledgements

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