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- > Synthesis of diethylcyanamide and cyanoguanidine complexes of manganese and rhenium.
- > The first bis(diethylcyanamide) complexes of manganese and rhenium were also prepared.

> Crystallographic characterization of two complexes is described.

Preparation of Diethylcyanamide and Cyanoguanidine Complexes of Manganese and Rhenium

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ABSTRACT

Diethycyanamide complexes $[M(N \equiv CNEt_2)(CO)_n L_{5\cdot n}]BPh_4$ (**1a–5a**) $[M = Mn, Re; n = 1, 2, 3; L = PPh(OEt)_2, P(OEt)_3]$ were prepared by allowing hydrides $MH(CO)_n L_{5\cdot n}$ to react first with triflic acid (HOTf) and then with an excess of diethylcyanamide. The related cyanoguanidine derivatives $[M\{N \equiv CN(H)C(NH_2) = NH\}(CO)_n L_{5\cdot n}]BPh_4$ (**1b–4b**) were prepared by reacting hydrides $MH(CO)_n L_{5\cdot n}$ first with an equivalent of HOTf and then with an excess of cyanamide $N \equiv CNH_2$ or, alternatively, with cyanoguanidine. Bis(diethylcyanamide) complexes $MBr(N \equiv CNEt_2)_2(CO)_3$ (**6**, **7**) were prepared by allowing pentacarbonyl species $MBr(CO)_5$ to react with an excess of cyanamide $N \equiv CNEt_2$. The complexes were characterised by spectroscopy (IR, ¹H, ³¹P, ¹³C NMR) and by X-ray crystal structure determination of $[Mn(N \equiv CNEt_2)(CO)_2\{PPh(OEt)_2\}_3]BPh_4$ (**2a**) and ReBr($N \equiv CNEt_2)_2(CO)_3$ (**7a**).

Keywords: Manganese; Rhenium; Diethylcyanamide; Cyanoguanidine; Synthesis

1. Introduction

The synthesis and reactivity of transition metal complexes containing cyanamide $N=CNR_2$ (R = H, alkyl, aryl) or its dimeric form, cyanoguanidine $N=CN(H)C(NH_2)=NH$, as ligands has been relatively little developed over the years [1-8], in spite of the close relationship with the nitrile RCN complexes [9] and the biological and synthetic interest [10] of these amino-functionalised nitrile species. Only a limited number of cyanamide and cyanoguanidine complexes of transition metals have been reported, mainly with molybdenum [7], platinum [6] or copper [5] as central metals. ACCEPTED MANUSCRIPT Instead, only two papers give reports for both manganese [11] and rhenium [12], involving Mn(η^5 -C₅H₅)(CO)₂(N=CNEt₂) and ReCl₂(N=CNEt₂)(PMePh₂)₃ derivatives, respectively.

We are interested in the chemistry not only of "diazo" complexes of transition metals with d^6 configuration [13], but also of nitrile derivatives [14] and, recently, diethylcyanamide and cyanoguanidine complexes of ruthenium and osmium [15]. We have now extended these studies on cyanamide derivatives to the manganese triad, and this paper reports the synthesis of the first cyanoguanidine and bis(diethylcyanamide) complexes of manganese and rhenium.

2. Experimental section

2.1. 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. $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were Pressure Chemical Co. (USA) products, used as received. The phosphane PPh(OEt)₂ was prepared by the method of Rabinowitz and Pellon [16], whereas triethoxyphosphane P(OEt)₃ was an Aldrich product, purified by distillation under nitrogen. 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 (¹H, ³¹P, ¹³C) were obtained on an AVANCE 300 Bruker spectrometer at temperatures between -90 and +30 °C, unless otherwise noted. ¹H and ¹³C{¹H} spectra are referred to internal tetramethylsilane; ³¹P{¹H} chemical shifts are reported with respect to 85% H₃PO₄; downfield shifts are considered positive. COSY, HMQC and HMBC NMR experiments were performed with standard programs. The iNMR software package [17] was used to process NMR data. The conductivity of 10⁻³ mol dm⁻³ solutions of the complexes in CH₃NO₂ 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).

2.2. Synthesis of complexes

Hydrides $MnH(CO)_nL_{5-n}$ (n = 3, 2, 1) and $ReH(CO)_nL_{5-n}$ (n = 3, 2) [$L = P(OEt)_3$, $PPh(OEt)_2$] were prepared following the previously reported methods [18,19].

2.2.1. $[Mn(N=CNEt_2)(CO)_nL_{5-n}]BPh_4(1a-3a) [n = 3 (1a), 2 (2a), 1 (3a); L = PPh(OEt)_2]$

A slight excess of triflic acid HOSO₂CF₃ (HOTf) (0.22 mmol, 20 µL) was added to a solution of the appropriate hydride MnH(CO)_nL_{5-n} (0.20 mmol) in 8 mL of CH₂Cl₂ cooled to -196 °C. The reaction mixture was allowed to reach the room temperature, stirred for 1 h, and then an excess of diethylcyanamide N=CNEt₂ (0.8 mmol, 93 µL) added. After 3 h of stirring, the solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of NaBPh₄ (0.28 mmol, 96 mg). A yellow solid slowly separated out from the resulting solution cooled to -25 °C, which was filtered and crystallised from ethanol; yield 0.137 g (72%) for **1a**, 0.177 g (79%) for **2a**, 0.220 g (85%) for **3a**.

1a: IR (KBr pellet) v_{CN} : 2258 (m); v_{CO} : 2062 (w), 1987, 1947 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C) δ: 7.65–6.89 (m, 30 H, Ph), 4.11, 4.01 (m, 8 H, CH₂ phos), 2.42 (q, 4 H, CH₂ cyanamide), 1.42 (t, 12 H, CH₃ phos), 0.80 (t, 6 H, CH₃ cyanamide) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C) δ: A₂ spin syst, 190.5 (s br); (CD₂Cl₂, -70 °C): $\delta = (A_2 \text{ spin syst})$ 191.1 (s) ppm. $\Lambda_M = 51.8 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. C₅₂H₆₀N₂BMnO₇P₂ (952.74): calcd. C 65.55, H 6.35, N 2.94; found C 65.37, H 6.42, N 3.03%.

2a: IR (KBr pellet) v_{CN} : 2253 (m); v_{CO} : 1978, 1897 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C) δ : 7.60–6.88 (m, 35 H, Ph), 4.15–3.75 (m, 12 H, CH₂ phos), 2.36 (q, 4 H, CH₂ cyanamide), 1.37, 1.35, 1.34 (t, 18 H, CH₃ phos), 0.80 (t, 6 H, CH₃ cyanamide) ppm. ³¹P{¹H} NMR (CD₂Cl₂, -70 °C) δ : A₂B spin syst, δ_A 197.3, δ_B 182.0, J_{AB} = 62.0 Hz. Λ_M = 55.1 Ω^{-1} mol⁻¹ cm². C₆₁H₇₅N₂BMnO₈P₃ (1122.93): calcd. C 65.24, H 6.73, N 2.49; found C 65.05, H 6.59, N 2.41%.

3a: IR (KBr pellet) v_{CN} : 2253 (m); v_{CO} : 1880 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C) δ : 7.58–6.88 (m, 40 H, Ph), 3.63 (m, 16 H, CH₂ phos), 2.77 (q, 4 H, CH₂ cyanamide), 1.18 (t, 24 H, CH₃ phos), 1.04 (t, 6 H, CH₃ cyanamide) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C) δ : A₄ spin syst, 200.0 (br); (CD₂Cl₂, -70 °C): δ = (A₄ spin syst) 197.2 (s br) ppm. Λ_M = 55.6 Ω^{-1} mol⁻¹ cm². C₇₀H₉₀N₂BMnO₉P₄ (1293.12): calcd. C 65.02, H 7.02, N 2.17; found C 64.84, H 7.16, N 2.06%.

2.2.2. $[Mn{N=CN(H)C(NH_2)=NH}(CO)_nL_{5-n}]BPh_4(1b, 2b) [n = 3 (1b), 2 (2b); L = PPh(OEt)_2]$

Method 1: A slight excess of HOTf (0.22 mmol, 20 μ L) was added to a solution of the appropriate hydride MnH(CO)_nL_{5-n} (0.20 mmol) in 8 mL of toluene cooled to -196 °C and the reaction mixture, brought to room temperature, was stirred for 1 h. An excess of cyanamide N=CNH₂ (0.8 mmol, 34 mg) in ethanol (5 mL) was added and the resulting mixture stirred for 24 h.

The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of NaBPh₄ (0.4 mmol, 137 mg). A white solid slowly separated out by cooling the resulting solution to -25 °C, which was filtered and crystallised from dichloromethane and ethanol; yield 0.122 g (65%) for **1b**, 0.133 g (60%) for **2b**.

Method 2: A An excess of HOTf (0.22 mmol, 20 μ L) was added to a solution of the appropriate hydride MnH(CO)_nL_{5-n} (0.20 mmol) in 8 mL of toluene cooled to -196 °C and the reaction mixture, brought to room temperature, was stirred for 1 h. An excess of cyanoguanidine N=CN(H)C(NH₂)=NH (0.4 mmol, 34 mg) in ethanol (5 mL) was added and the resulting mixture stirred for 24 h. The solvent was removed under reduced pressure to give an oil, which was treated with ethanol (2 mL) containing an excess of NaBPh₄ (0.4 mmol, 137 mg). A white solid slowly separated out by cooling the resulting solution to -25 °C, which was filtered and crystallised from dichloromethane and ethanol; yield 0.143 g (76%) for **1b**, 0.164 g (74%) for **2b**.

1b: IR (KBr pellet) v_{NH} : 3456, 3407, 3326 (m); v_{CN} : 2237 (m); v_{CO} : 2059 (m), 1972, 1942 (s); δ_{NH2}: 1632 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C) δ: 7.65–6.89 (m, 30 H, Ph), 4.06, 3.96 (m, 8 H, CH₂), 3.51 (s br, 4 H, NH+NH₂ cyanamide), 1.38 (t, 12 H, CH₃); (CD₂Cl₂, -70 °C): δ = 7.55–6.89 (m br, 30 H, Ph), 3.96, 3.84 (br, 8 H, CH₂), 3.09, 2.29 (br, 4 H, NH+NH₂ cyanamide), 1.29 (t br, 12 H, CH₃) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C) δ: A₂ spin syst, 189.5 (s br); (CD₂Cl₂, -70 °C): δ = (A₂ spin syst) 189.6 (s) ppm. Λ_M = 53.2 Ω⁻¹ mol⁻¹ cm². C₄₉H₅₄N₄BMnO₇P₂ (938.67): calcd. C 62.70, H 5.80, N 5.97; found C 62.58, H 5.92, N 6.11%.

2b: IR (KBr pellet) v_{NH} : 3502 (w), 3439, 3389, 3367 (m); v_{CN} : 2247 (m); v_{CO} : 1967, 1903 (s); δ_{NH_2} : 1623 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C) δ : 7.50–6.88 (m, 35 H, Ph), 3.96, 3.83, 3.73, 3.67 (m, 12 H, CH₂), 3.47 (s br, 4 H, NH+NH₂ cyanamide), 1.32, 1.31, 1.27 (t, 18 H, CH₃); (CD₂Cl₂, -70 °C): δ = 3.55, 2.13 (br, 4 H, NH+NH₂ cyanamide) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 20 °C) δ : 222.1, 219.6 (m br, CO), 165–122 (m, Ph), 63.10 (m, CH₂), 58.6 (s, C=NH), 16.48 (m, CH₃) ppm. ³¹P{¹H} NMR (CD₂Cl₂, -70 °C) δ : A₂B spin syst, δ_A 195.7, δ_B 182.8, J_{AB} = 58.3 Hz. Λ_M = 52.7 Ω^{-1} mol⁻¹ cm². C₅₈H₆₉N₄BMnO₈P₃ (1108.86): calcd. C 62.82, H 6.27, N 5.05; found C 63.00, H 6.17, N 4.96%.

2.2.3. $[Re(N=CNEt_2)(CO)_3\{PPh(OEt)_2\}_2]BPh_4$ (4a) and $[Re(N=CNEt_2)(CO)_2\{P(OEt)_3\}_3]BPh_4$ (5a)

A slight excess of HOTf (0.165 mmol, 15 μ L) was added to a solution of the appropriate hydride ReH(CO)_{*n*}L_{5-*n*} (0.15 mmol) in 8 mL of CH₂Cl₂ cooled to -196 °C and the reaction mixture,

brought to room temperature, was stirred for 1 h. An excess of diethylcyanamide N=CNEt₂ (0.75 mmol, 87 μ L) was added and the reaction mixture stirred for 24 h. The solvent was removed under reduced pressure to give an oil, which was treated with ethanol (2 mL) containing an excess of NaBPh₄ (0.3 mmol, 103 mg). A pale-yellow solid slowly separated out by cooling the resulting solution to -25 °C, which was filtered and crystallised from ethanol; yield 0.137 g (84%) for **4a**, 0.141 g (81%) for **5a**.

4a: IR (KBr pellet) v_{CN} : 2260 (m); v_{CO} : 2068 (w), 1980, 1942 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C) δ: 7.65–6.88 (m, 30 H, Ph), 4.03, 3.96 (m, 8 H, CH₂ phos), 2.56 (q, 4 H, CH₂ cyanamide), 1.40 (t, 12 H, CH₃ phos), 0.87 (t, 6 H, CH₃ cyanamide) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C) δ: A₂ spin syst, 134.8 (s br); (CD₂Cl₂, -70 °C): $\delta = (A_2 \text{ spin syst})$ 136.25 (s) ppm. $A_M = 52.5 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$. C₅₂H₆₀N₂BO₇P₂Re (1084.01): calcd. C 57.62, H 5.58, N 2.58; found C 57.39, H 5.46, N 2.64%.

5a: IR (KBr pellet) v_{CN} : 2264 (m); v_{CO} : 1905, 1892 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C) δ: 7.32–6.88 (m, 20 H, Ph), 4.05 (m, 18 H, CH₂ phos), 3.09 (q, 4 H, CH₂ cyanamide), 1.34, 1.32 (t, 27 H, CH₃ phos), 1.25 (t, 6 H, CH₃ cyanamide) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 20 °C) δ: 193.58 (td, CO, $J_{CP} = 11.3$, $J_{CP} = 2.3$ Hz), 191.94 (td, CO, $J_{CP} = 80.0$, $J_{CP} = 8.3$ Hz), 165–122 (m, Ph), 66.04 (s, C≡N), 62.05 (m, CH₂ phos), 46.7 (s, CH₂ cyanamide), 16.32 (m, CH₃ phos), 13.37 (s, CH₃ cyanamide) ppm. ³¹P{¹H} NMR (CD₂Cl₂, -30 °C) δ: A₂B spin syst, δ_A 115.6, δ_B 114.4, $J_{AB} = 47.5$ Hz. $\Lambda_M = 53.0 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$. $C_{49}H_{75}N_2BO_{11}P_3Re$ (1158.07): calcd. C 50.82, H 6.53, N 2.42; found C 50.65, H 6.63, N 2.35%.

2.2.4. $[Re\{N \equiv CN(H)C(NH_2) = NH\}(CO)_3\{PPh(OEt)_2\}_2]BPh_4(4b)$ and $[Re\{N \equiv CN(H)C(NH_2) = NH\}-(CO)_2\{P(OEt)_3\}_3]BPh_4(5b)$

Method 1: An excess of HOTf (0.165 mmol, 15 μ L) was added to a solution of the appropriate hydride ReH(CO)_{*n*}L_{5-*n*} (0.20 mmol) in 8 mL of CH₂Cl₂ cooled to -196 °C and the reaction mixture, brought to room temperature, was stirred for 1 h. An excess of cyanamide N=CNH₂ (0.6 mmol, 25 mg) in ethanol (5 mL) was added and the resulting mixture stirred for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (2 mL) containing an excess of NaBPh₄ (0.3 mmol, 103 mg). A pale-yellow solid slowly separated out by cooling the resulting solution to -25 °C, which was filtered and crystallised from dichloromethane and ethanol; yield 0.170 g (80%) for **4b**, 0.195 g (85%) for **5b**.

Method 2: The complex was prepared exactly like with Method 1, but using cyanoguanidine (0.3 mmol, 25 mg) as a reagent; yield 0.175 g (82%) for **4b**, 0.195 g (85%) for **5b**.

4b: IR (KBr pellet) v_{NH} : 3493 (w), 3411, 3322 (m); v_{CN} : 2240 (m); v_{CO} : 2061 (w), 1972, 1955 (s); δ_{NH_2} : 1632 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C) δ: 7.62–6.88 (m, 30 H, Ph), 4.28 (br, 4 H, NH+NH₂ cyanamide), 4.06, 3.99 (m, 8 H, CH₂), 1.37 (t, 12 H, CH₃); (CD₂Cl₂, -30 °C): δ = 7.60–6.97 (m, 30 H, Ph), 4.03, 3.88 (m br, 8 H, CH₂), 3.77, 2.78 (br, 4 H, NH+NH₂ cyanamide), 1.38 (t, 12 H, CH₃) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 20 °C) δ: A₂ spin syst, 134.0 (s); (CD₂Cl₂, -30 °C): δ = (A₂ spin syst) 134.4 (s) ppm. Λ_{M} = 52.6 Ω⁻¹ mol⁻¹ cm². C₄₉H₅₄N₄BO₇P₂Re (1069.94): calcd. C 55.01, H 5.09, N 5.24; found C 54.82, H 5.18, N 5.15%.

5b: IR (KBr pellet) v_{NH} : 3529, 3440, 3344 (m); v_{CN} : 2247 (m); v_{CO} : 1981, 1900 (s); δ_{NH_2} : 1634 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C) δ: 7.52–6.88 (m, 20 H, Ph), 4.78 (m, 4 H, NH+NH₂ cyanamide), 4.12 (m, 18 H, CH₂), 1.40, 1.39 (t, 27 H, CH₃); (CD₂Cl₂, -70 °C): δ = 7.53–7.07 (m, 20 H, Ph), 4.99, 4.31 (br, 4 H, NH+NH₂ cyanamide), 4.10, 3.87 (br, 18 H, CH₂), 1.41, 1.39 (t, 27 H, CH₃) ppm. ³¹P{¹H} NMR (CD₂Cl₂, -70 °C) δ: AB₂ spin syst, δ_A 119.2, δ_B 116.5, J_{AB} = 46.2 Hz. Λ_M = 54.4 Ω⁻¹ mol⁻¹ cm². C₄₆H₆₉N₄BO₁₁P₃Re (1144.00): calcd. C 48.29, H 6.08, N 4.90; found C 49.07, H 6.00, N 5.12%.

2.2.5. $fac-MnBr(N=CNEt_2)_2(CO)_3$ (6a)

An excess of diethylcyanamide (1.8 mmol, 209 μ L) was added to a solution of the pentacarbonyl complex MnBr(CO)₅ (100 mg, 0.36 mmol) in toluene (8 mL) and the reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure to give an oil, which was triturated with ethanol (3 mL). A pale-yellow solid slowly separated out by cooling the resulting solution to -25 °C, which was filtered and crystallised from dichloromethane and ethanol; yield 130 mg (87%). IR (KBr pellet) ν_{CN} : 2264 (m); ν_{CO} : 2033 (m), 1930, 1910 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C) δ : 3.19 (q, 8 H, CH₂), 1.32 (t, 12 H, CH₃) ppm. C₁₃H₂₀N₄BrMnO₃ (415.16): calcd. C 37.61, H 4.86, N 13.50; found C 37.79, H 4.75, N 13.37%.

2.2.6. fac-ReBr(N=CNEt₂)₂(CO)₃ (7a)

An excess of diethylcyanamide (1.23 mmol, 143 μ L) was added to a solution of the pentacarbonyl complex ReBr(CO)₅ (100 mg, 0.25 mmol) in toluene (8 mL) and the reaction mixture was refluxed for 5 h. The solvent was removed under reduced pressure to give an oil, which was

triturated with ethanol (3 mL). A white solid slowly separated out by cooling the resulting solution to -25 °C, which was filtered and crystallised from dichloromethane and ethanol; yield 116 mg (85%). IR (KBr pellet) v_{CN} : 2264 (m); v_{CO} : 2023 (m), 1917, 1897 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C) δ : 3.17 (q, 8 H, CH₂), 1.33 (t, 12 H, CH₃) ppm. C₁₃H₂₀N₄BrO₃Re (546.43): calcd. C 28.57, H 3.69, N 10.25; found C 28.43, H 3.80, N 10.12%.

2.2.6. mer-cis-ReBr(N=CNEt₂)₂(CO)₃ (7a₁)

In a 25-mL three-necked round-bottomed flask were placed 80 mg (0.15 mmol) of *fac*-ReBr(N=CNEt₂)₂(CO)₃ (**7a**), an excess of NaBPh₄ (0.2 mmol, 68 mg) and 10 mL of ethanol. The reaction mixture was stirred for 2 h and then the solvent removed under reduced presure to about 2 mL. By cooling the reaction mixture to -25 °C, a pale-yellow solid separated out, which was filtered and dried under vacuum; yield 72 mg (90%). IR (KBr pellet) v_{CN} : 2264 (m); v_{CO} : 2034 (w), 1928, 1872 (s) cm⁻¹. ¹H NMR (CD₂Cl₂, 20 °C) δ : 3.11, 3.02 (q, 8 H, CH₂), 1.27, 1.23 (t, 12 H, CH₃) ppm. C₁₃H₂₀N₄BrO₃Re (546.43): calcd. C 28.57, H 3.69, N 10.25; found C 28.69, H 3.75, N 10.12%.

2.3. X-ray Crystallography

Crystallographic data were collected (at room temperature for **2a** and at low temperature for **7a**) on a Bruker Smart 1000 CCD diffractometer at CACTI (Universidade de Vigo) using graphite monochromated Mo-K \langle radiation ($\lambda = 0.71073$ Å), and were corrected for Lorentz and polarisation effects. The software SMART [20] was used for collecting frames of data, indexing reflections, and the determination of lattice parameters, SAINT [21] for integration of intensity of reflections and scaling, and SADABS [22] for empirical absorption correction. The crystallographic treatment was performed with the Oscail program [23]. The structures were solved by Patterson method and refined by a full-matrix least-squares based on F² [24]. Non-hydrogen atoms were refined with anisotropic displacement parameters. The NEt₂ fragment of the dialkylcyanamide groups are usually disorder [25], so for **2a** it was necessary to apply some restrains. The SADI instruction was applied for fix C–C and C–N lengths. Details of crystal data and structural refinement are given in Table 1. CCDC 981666-981667 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

3.1. Preparation of diethylcyanamide and cyanoguanidine complexes

Diethylcyanamide complexes of manganese and rhenium $[M(N \equiv CNEt_2)(CO)_n L_{5-n}]BPh_4$ (1a– 5a) were prepared by reacting hydrides $MH(CO)_n L_{5-n}$ first with triflic acid (HOTf) and then with an excess of N=CNEt₂, as shown in Scheme 1.



Scheme 1. M = Mn (1, 2, 3a), Re (4, 5); L = PPh(OEt)₂ (1–4), P(OEt)₃ (5)

The reaction of the hydride MH(CO)_{*n*}L_{5-*n*} (n = 2, 3) with triflic acid is known to proceed with the formation of dihydrogen complex [M(η^2 -H₂)(CO)_{*n*}L_{5-*n*}]⁺ which, by loss of H₂, yields the triflate intermediate M(κ^1 -OTf)(CO)_{*n*}L_{5-*n*} [18,19]. Substitution of the triflate ligand by N=CNEt₂ afforded the final diethylcyanamide complexes **1a**, **2a**, **4a**, **5a**, which were separated as BPh₄⁻ salts and characterised.

The related monocarbonyl MnH(CO)L₄ was also reacted with triflic acid to give the stable dihydrogen cation $[Mn(\eta^2-H_2)(CO)L_4]^+$ [18], which underwent substitution of the η^2-H_2 group by N=CNEt₂ yielding the final diethylcynamide derivative $[Mn(N=CNEt_2)(CO)L_4]BPh_4$ (**3a**).

The related cyanoguanidine complexes $[M{N=CN(H)C(NH_2)=NH}(CO)_nL_{5\cdot n}]BPh_4$ (1b–5b)

were prepared following two different methods involving, in one case, the reaction of hydrides $MH(CO)_nL_{5-n}$ first with an equivalent of triflic acid and then with an excess of cyanamide N=CNH₂, as shown in Scheme 2.



Scheme 2. L = M = Mn (1, 2), Re (4, 5); $L = PPh(OEt)_2 (1, 2, 4)$, P(OEt)₃ (5)

Alternatively, the cyanoguanidine complexes were prepared by reacting hydrides $MH(CO)_nL_{5-n}$ first with HOTf and then with an excess of free cyanoguanidine $N=CN=C(NH_2)_2$ in ethanol.

The formation of complexes **1b**, **2b**, **4b**, **5b** from the reaction with cyanamide was not unexpected, in view of the known ease of dimerisation of N=CNH₂. The initial coordination of N=CNH₂ to the metal fragment, giving $[M(N=CNH_2)(CO)_nL_{5-n}]^+$, may be followed by nucleophilic attack by a second N=CNH₂ on the cyanamide carbon atom of the coordinate cyanamide yielding, after H-shift, the N-imine-bonded cyanoguanidine complexes

 $[M{N(H)=C(NH_2)N(H)C=N}(CO)_nL_{5-n}]^+$. Linkage isomerisation of this ligand gave the final N-nitrile-bonded derivatives **1b**, **2b**, **4b**, **5b**.

Cyanamide and cyanoguanidine complexes of the manganese triad are very rare and, to the best of our knowledge, only one example of both manganese [11] and rhenium [12] diethylcyanamide complexes have been reported, and none for cyanoguanidine. The use as precursors of mixed-ligand hydride complexes $MH(CO)_nL_{5-n}$, containing phosphanes and carbonyls, allowed easy synthesis of both diethylcyanamide and cyanoguanidine complexes of Mn and Re.

It is worth noting that the cyanamide and cyanoguanidine complexes of both Mn and Re (1–4) were all prepared with phenyldiethoxyphosphane PPh(OEt)₂ as supporting ligand. Instead, rhenium dicarbonyls [Re(N=CNEt₂)(CO)₂L₃]BPh₄ (**5a**) and [Re{N(H)=C(NH₂)N(H)C=N}(CO)₂L₃]BPh₄ (**5b**) were obtained with triethoxyphosphane P(OEt)₃ as supporting ligand.

Complexes 1–5 were all isolated as white or yellow solids stable in air and in solution of polar organic solvents, where they behave as 1:1 electrolytes [26]. Their characterisation is supported by analytical and spectroscopic (IR, NMR) data and by X-ray crystal structure determination of complex [Mn(N=CNEt₂)(CO)₂{PPh(OEt)₂}₃]BPh₄ (**2a**), the ORTEP [27] of which is shown in Figure 1.



Figure 1. ORTEP view of the cation **2a**, drawn at 30% probability level. Phenyl and ethoxy groups on all the phosphanes were not drawn for clarity.

The compound consists of a tetraphenylborate anion (not shown in figure) and a manganese cation complex. In the cation, the manganese atom is coordinated by two carbonyl ligands, three PPh(OEt)₂ ligands and a N,N-diethylcyanamide ligand N≡CNEt₂. The overall geometry is best described as octahedral, and the arrangement around the metal is such that the phosphane ligands are in *meridional* disposition. Consequently, both carbonyl ligands are *cis* arranged and the cyanamide ligand is *trans* to a carbonyl ligand. Some distortion arises because of the bending of the mutually *trans* phosphanes towards the carbonyl ligand, doubtless due to the steric requirements of the phosphanes. This distortion gives a P-Mn-P trans angle of 170.22(4)°. The other two trans angles are 178.46(14) and 176.84(10)°, and the *cis* angles range from 84.21(11) to 95.82(5)°. The Mn–C carbonyl bond length *trans* to the phosphane ligand is slightly longer than that *trans* to the cyanamide ligand, 1.801(4) Å vs 1.758(3) Å. The Mn–P bond lengths of the mutually phosphane ligands, 2.2618(18) and 2.2722(17) Å, are slightly shorter than that *trans* to the carbonyl ligand, 2.2945(19) Å. The Mn–N bond length, 2.002(3) Å, *trans* to a carbonyl ligand, is longer than that found in $Mn(\eta^5-C_5H_5)(CO)_2(N=CNEt_2)$, 1.977(2) Å [11]. It is worth noting that such half-sandwich compound is the first N,N-diethylcyanamide manganese complex to be crystallographically described¹ and, at the moment of writing this paper, there are no others in the CCDC database [28].

The N,N-diethylcyanamide ligand shows a C(1)-N(1)-Mn bond angle of 175.6(3)°, and a N(1)-C(1)-N(2) bond angle of 175.5(5)°, matching the sp character of C(1), as confirmed by the N(1)–C(1) bond length of only 1.133(4) Å, as expected for a triple bond [29]. The N(2)–C(1) bond length, 1.300(5) Å, matches a double bond length [29] and is similar to that found in other N,N-diethylcyanamide complexes, for example, Mn(η^5 -C₅H₅)(CO)₂(N=CNEt₂) [11] or [Ru(NH₂^{*i*}Pr)(NCNEt₂){P(OEt)₃}₄](BPh₄)₂ [15b]. These values show conjugation between the nitrogen NEt₂ lone pair and the C=N π bond [1]. It has been stated that η^1 -bound NCNR₂ species can adopt a bent or linear form in the complexes and that the linear coordination mode (M-N-C angle of 176–180°) is more common in transition metal complexes. For compound **2a**, the angle, 175.5(5)°, falls within the lower limit for linear coordination mode, perhaps due to the *trans* coordination of a carbonyl ligand. It is believed that the *trans* influence enhances the significance of the bent M-N=C=NEt₂ structure (**A**) shown in Scheme 3 [1,30].



Scheme 3.

Also worthy of note is the trigonal planar coordination around the amino N-atom of the diethylcyanamide ligand [the sum of the angles around N(2) is 357.6°]. This feature has also been found in Mn(η^5 -C₅H₅)(CO)₂(N=CNEt₂) [11] and in other dialkylcyanamide complexes, and is interpreted as a consequence of the delocalisation of the amide lone pair of electrons and the significant contribution of sp² hybridised N resonance [1,30,31].

The IR spectra of diethylcyanamide complexes $[M(N\equiv CNEt_2)(CO)_3 \{PPh(OEt)_2\}_2]BPh_4$ (1a, 4a) show a strong band at 2260–2258 cm⁻¹, attributed to the v_{CN} of the nitrile group. In addition, in the CO stretching region between 2068 and 1942 cm⁻¹, three bands appear – one of medium intensity and two strong – indicating a *mer* arrangement of the three carbonyl ligands. In the temperature range +20 to -80 °C, the ³¹P NMR spectra show a sharp singlet, indicating the magnetic equivalence of the two phosphanes. On this basis, *mer-trans* geometry I (Scheme 1) is proposed for tricarbonyl derivatives 1a and 4a. As well as the signals of the phosphanes and BPh₄⁻ anion, the ¹H NMR spectra show a quartet and a triplet of ethyl substituents of cyanamide, matching the proposed formulation for the complexes. Besides the strong v_{CN} band of the N=CNEt₂ group at 2264–2253 cm⁻¹, the IR spectra of dicarbonyl compounds [M(N=CNEt₂)(CO)₂{PPh(OEt)₂}₃]BPh₄ (**2a**, **5a**) show two strong v_{CO} bands at 1978–1905 and 1897–1892 cm⁻¹, attributed to two carbonyl ligands in a mutually *cis* position. The ¹³C NMR spectrum of **5a** also indicates that the two CO groups are not magnetically equivalent, since they show two triplets of doublets in the carbonyl carbon region, at 193.58 and 191.94 ppm. At 203 K, the ³¹P NMR spectra of complexes **2a** and **5a** display an A₂B multiplet, indicating that two phosphanes are magnetically equivalent and different from the third. On this basis, *mer-cis* geometry **II**, like that found in the solid state, is proposed for dicarbonyl derivatives **2a** and **5a**.

The IR spectrum of the monocarbonyl compound $[Mn(N=CNEt_2)(CO){PPh(OEt)_2}_4]BPh_4$ (**3a**) shows v_{CN} at 2253 cm⁻¹ and v_{CO} at 1880 cm⁻¹. The ¹H NMR spectrum supports the presence of the diethylcyanamide ligand, showing the quartet at 2.77 ppm and the triplet at 1.18 ppm of the ethyl substituents of the cyanamide. In the temperature range +20 to -80 °C, the ³¹P NMR spectra show only one singlet, indicating the magnetic equivalence of the four phosphane ligands. On this basis, *trans* geometry **III** (Scheme 1) is proposed for monocarbonyl derivative **3a**.

The IR spectra of cyanoguanidine derivatives $[M{N=CN(H)C(NH_2)=NH}(CO)_3L_2]BPh_4$ (**1b**, **4b**) show the v_{NH} absorptions of the NH and NH₂ groups at 3493–3322 cm⁻¹, whereas v_{CN} appears as one medium-intensity band at 2237–2240 cm⁻¹ for both Mn and Re derivatives. The presence of only one v_{CN} absorption also indicates that the cyanoguanidine ligand is present in the amine form. In addition, δ_{NH_2} is observed as a strong band at 1632 cm⁻¹ while the CO stretching region has three bands – one of medium intensity and two strong – also present at 2061–1942 cm⁻¹, indicating a *mer* arrangement for the three carbonyl ligands.

Besides the characteristic signals of the phosphanes and BPh_4^- anion, the ¹H NMR spectra show either a broad signal at 3.51 ppm (**1b**) or two at 4.28 and 4.06 ppm (**4b**), attributed to the NH₂ and NH protons of cyanoguanidine. However, when sample temperature is lowered, the profiles of the spectra change and, at -70 °C, two broad signals at 3.09 and 2.29 appear for **1b**, and at 2.78 and 3.77 ppm, with an intensity ratio of 2:1, for **4b**, attributed to the NH₂ protons and one NH proton of cyanoguanidine. The other NH signal is probably masked by the methylene protons of phosphane. In the temperature range +20 to -70 °C, the ³¹P NMR spectra show only one singlet, indicating the magnetic equivalence of the two phosphane ligands. On this basis, *mer-trans* geometry **IV** (Scheme 2) is proposed for cyanoguanidine complexes **1b** and **4b**. The IR spectra of dicarbonyl derivatives $[M{N=CN(H)C(NH_2)=NH}(CO)_2L_3]BPh_4$ (**2b**, **5b**) show the v_{NH} of the cyanoguanidine at 3529–3344 cm⁻¹, v_{CN} falls to 2247 cm⁻¹ and δ_{NH_2} is observed as a strong band at 1634–1623 cm⁻¹. Two v_{CO} bands also appear at 1981–1967 and 1903–1900 cm⁻¹, attributed to two carbonyls in mutually *cis* position.

The ¹³C NMR spectrum of **2b** indicates that the two CO ligands are magnetically nonequivalent, showing two signals in the carbonyl carbon region at 219.6 and 222.1 ppm. The signals of the phosphanes and BPh₄⁻ anion, and a singlet at 58.6 ppm attributed to the resonance of the $C(NH_2)=NH$ group of cyanoguanidine, are also present. The ¹H NMR spectra confirm the presence of the cyanoguanidine ligand showing, at -70 °C, two broad signals at 3.55 and 2.13 ppm (Mn) and at 4.99 and 4.31 ppm (Re), with an intensity ratio of 1:2, attributed to one NH and the NH₂ groups of the N=CN(H)C(NH₂)=NH ligand. In the temperature range +20 to -80 °C, the ³¹P spectra show either an AB₂ or A₂B multiplet, indicating that two phosphanes are magnetically equivalent and different from the third. On this basis, *mer-cis* geometry V (Scheme 2) is proposed for cyanoguanidine derivatives **2b** and **5b**.

3.2. Preparation of bis(diethylcyanamide) complexes

Results from the phosphane-carbonyl mixed-ligand fragments $M(CO)_n L_{5-n}$ prompted us to extend study of diethylcyanamide and cyanoguanidine to the simple carbonyl compounds $MBr(CO)_5$ (M = Mn, Re). The reaction with diethylcyanamide proceeds with substitution of the carbonyl ligands, giving bis(derivatives) $MBr(N=CNEt_2)_2(CO)_3$ (**6a**, **7a**), which were isolated in good yield and characterised (Scheme 4).



Scheme 4. M = Mn (6a), Re (7a).

Although the reaction proceeded at room temperature with manganese, reflux conditions were required for rhenium. However, only bis(diethylcyanamide) complexes **6a** and **7a** were obtained from this reaction: the addition of an equimolar amount of $N=CNEt_2$ did not yield monocyanamide derivatives of the type $MBr(N=CNEt_2)(CO)_4$, but a mixture of bis-complexes **6a** and **7a** and the starting $MBr(CO)_5$ compounds. It is probable that substitution of one carbonyl in the

monocyanamide species $MBr(N=CNEt_2)(CO)_4$ is faster than that in $MBr(CO)_5$, mainly yielding bisones $MBr(N=CNEt_2)_2(CO)_3$. In addition, reflux conditions for Mn, or longer reaction times for Re, did not afford any tris(cyanamide) $MBr(N=CNEt_2)_3(CO)_2$ species, but only mixtures of biscomplexes and decomposition products. Pentacarbonyl compounds $MBr(CO)_5$ were also treated with both cyanamide $N=CNH_2$ and cyanoguanidine, but no pure compounds resulted, the isolated products being intractable mixtures. Therefore, it seems that only bis(diethylcyanamide) complexes **6a** and **7a** can be obtained from the reaction of $MBr(CO)_5$ with cyanamide.

Bis(cyanamide) complexes of transition metals are very rare [5c,6c,32] and involve only Pt [6c,32a,b], Ru [32c] and Cu [5c] derivatives. The reaction of pentacarbonyl compounds MBr(CO)₅ with diethylcyanamide allows the preparation of the first examples of bis(cyanamide) derivatives of the manganese triad.

Complexes MBr(N=CNEt₂)₂(CO)₃ (**6a**, **7a**) were isolated as pale-yellow (**6a**) or white (**7a**) solids, stable in air and in solution of common organic solvents, where they behave as non-electrolytes [26]. Their formulation is supported by analytical and spectroscopic (IR, NMR) data and by X-ray crystal structure determination of complex ReBr(N=CNEt₂)₂(CO)₃ (**7a**), the ORTEP [27] of which is shown in Figure 2.



Figure 2. ORTEP view of **7a** drawn at 30% probability level. Phenyl and ethoxy groups on all the phosphanes were not drawn for clarity.

The compound consists of a rhenium atom coordinated by one bromine ligand, three carbonyl ligands, and two N,N-diethylcyanamide ligands. The overall geometry is best described as octahedral, and the arrangement around the metal is such that the carbonyl ligands are in *facial*

disposition. Consequently, both cyanamide ligands are *cis*-disposed. The Re–C carbonyl bond distances are in the range 1.903(4) to 1.917(4) Å, the shorter one corresponding to that which is *trans* to the bromine ligand, but they do not show significant differences. The *trans* influence of the cyanamide ligand is comparable with the σ -donor bromine ligand, as previously reported [12,33]. The Re–Br bond length, 2.6191(5) Å, is close to the mean value found in the CCDC database [34].

To the best of our knowledge [28], only one cyanamide rhenium complex has been crystallographically described, the already-mentioned Re(II) complex *mer*-ReCl₂(NCNEt₂)(PMePh₂)₃ [12]. The latter has a Re–N distance of 2.109(5) Å, *trans* to a phosphane ligand. Complex **7a** shows two Re–N(cyanamide) bond lengths of 2.142(3) and 2.138(3) Å, *trans* to a carbonyl ligand. Although these values are longer than that of the Re(II) complex *mer*-ReCl₂(NCNEt₂)P₃, they are comparable to other *trans* carbonyl-nitrile Re(I) complexes, like the values of 2.145(7) Å in [Re(N,N'-terpy)(CO)₃(CH₃CN)]PF₆ [35] or 2.151(7) Å in [Re(CO)₃(CH₃CN){H(pzAn^{Me})}]PF₆ [36].

As in **2a** (see above) or other N,N-diethylcyanamide complexes [1,15b] these ligands have average C-N-Re bond angles of 172.7(3)° and a N-C-N bond angles of 177.5(4)°. Again, the cyanamide moiety shows extensive electronic delocalisation, and the C–N bond lengths alternatively match triple [1.146(5), 1.148(5) Å] and double bonds [1.304(5), 1.308(5) Å]. The amine nitrogen atoms also display a distorted trigonal-planar geometry, as demonstrated by the sum of angles of 356.5(3) and 359.5(3)°. It is worth noting that, in the Re(II) compound *mer*-ReCl₂(NCNEt₂)(PMePh₂)₃ [12] the coordination around this atom is described as trigonalpyramidal.

The average C-N-Re bond angles of 172.7(3)° [171.8(3) and 173.6(3)°] lie both out of the range (180–176°) proposed for linear arrangement and out of the values proposed for bent coordination (M–N–C \leq 170°), being more acute than the value found for the Re(II) compound *mer*-ReCl₂(NCNEt₂)(PMePh₂)₃ [12], 174.3(6)°. Again as in **2a**, the *trans* influence of the carbonyl groups may explain this bending.

In the carbonyl stretching region, the IR spectra of bis(diethylcyanamide) complexes $MBr(N \equiv CNEt_2)_2(CO)_3$ (**6a**, **7a**) show three strong bands at 2033, 1930 and 1910 cm⁻¹ (**6a**) and 2023, 1917 and 1897 cm⁻¹ (**7a**), indicating a *fac* arrangement of the carbonyl ligands. A strong band at 2264 cm⁻¹ also appears in the spectra of **6a** and **7a**, and was attributed to the v_{CN} of the diethylcyanamide ligand. The presence of only one band is rather surprising, as the two cyanamides must be in mutually *cis* position and should thus show two v_{CN} bands. The v_{CN} values of the *cis*

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cyanamides are probably so close that the instrument could only detect one slightly broad signal. The ¹H NMR spectra of **6a** and **7a** confirm the presence of the diethylcyanamide ligands, showing one quartet at 3.19–3.17 ppm and one triplet at 1.33–1.32 ppm of their ethyl substituents. The presence of only a single signal (one quartet and one quintet) indicates the magnetic equivalence of the two N=CNEt₂ ligands. On this basis, *fac* geometry **VI**, like that found in the solid state for **7a**, may be proposed in solution for the bis(diethylcyanamide) derivatives **6a** and **7a**.

In ethanol solution containing NaBPh₄, complex *fac*-ReBr(N=CNEt₂)₂(CO)₃ (**7a**) slowly isomerised to give the *mer-cis* derivative **7a**₁, which was isolated as a white solid and characterised (Scheme 5).



Scheme 5.

Crucial for the *fac-mer* isomerisation of **7** was the presence of the NaBPh₄ salt which, by rendering the bromide ligand labile, may favour rearrangement of the ligands. This isomerisation is not surprising, owing to the large number of known rhenium complexes having *mer* geometry [37].

The IR spectrum of **7a**₁ shows three v_{CO} bands, one of medium intensity at 2034 cm⁻¹ and two strong ones at 1928 and 1872 cm⁻¹, indicating a *mer* arrangement of of the three carbonyl groups. The spectrum also displays a band of medium intensity at 2264 cm⁻¹, attributed to the v_{CN} of the diethylcyanamide ligands. The presence of these ligands was confirmed by the ¹H NMR spectrum, which shows two quartets at 3.11 and 3.02 ppm and two triplets at 1.27 and 1.23 ppm of the ethyl substituents of N=CNEt₂. Such a pattern also indicates that the two cyanamide ligands are magnetically non-equivalent. On this basis, *mer-cis* geometry **VII** is proposed for complex **7a**₁. As observed in the related complex **7a**, the presence of only one v_{CN} band for two N=CNEt₂ groups in mutually *cis* position may be because the two v_{CN} have such close values that only a single band is visible in the spectrum.

4. Conclusions

In this report we describe the preparation of diethylcyanamide and cyanoguanidine complexes

of manganese and rhenium stabilised by the mixed-ligand fragment $M(CO)_n L_{5-n}$, containing phosphanes and carbonyls as supporting groups. The synthesis of the first bis(diethylcyanamide) derivatives $MBr(N \equiv CNEt_2)_2(CO)_3$ of manganese and rhenium is reported. The structural parameters of both mono- and bis(diethylcyanamide) complexes were also determined.

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Table 1. Crystal data and structure refinement for complexes **2a** and **7a**.

Identification code Empirical formula Formula weight Temperature Wavelength Crystal system Space group	2a $C_{61}H_{75}BMnN_2O_8P_3$ 1122.89 293(2) K 0.71073 Å Triclinic P-1	7a $C_{13}H_{20}BrN_4O_3Re$ 546.44 100(2) K 0.71073 Å Monoclinic C2/c
Unit cell dimensions	a = 11.114(10) A b = 15.082(14) Å c = 18.021(16) Å $\alpha = 86.985(14)^{\circ}$ $\beta = 84.740(14)^{\circ}$ $\gamma = 82.889(16)^{\circ}$	a = 17.461(3) A b = 16.463(3) Å c = 14.343(2) Å $\alpha = 90^{\circ}$ $\beta = 119.469(2)^{\circ}$ $\gamma = 90^{\circ}$
Volume	2982(5) Å ³	3589.6(10) Å ³
Z	2	8
Density (calculated)	1.251 Mg/m^3	2.022 Mg/m ³
Absorption coefficient	0.356 mm	9.012 mm
F(000)		2080 0.28 × 0.15 × 0.00 mm
Crystal size	$0.46 \times 0.41 \times 0.29 \text{ mm}$	$0.38 \times 0.15 \times 0.09 \text{ mm}$
le fange for data collection	$2.26 \text{ to } 25.69^{\circ}$	$1.82 \text{ to } 27.99^{\circ}$
Index ranges	$-13 \le h \le 13$	$-23 \le n \le 22$
	$-1/\leq K \leq 18$	$-21 \leq K \leq 21$
	$-21 \le 1 \le 21$	$-18 \le 1 \le 18$
Reflections collected	43930 11062 [D(int) 0.0207]	10193
Independent reflections	11063 [R(int) = 0.0397]	4285 [R(int) = 0.0472]
Reflections observed (>25)	/506	3001
Data Completeness	0.975	
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.7052	0.4038 and 0.1879
Refinement method	Full-matrix least-squares on F	Full-matrix least-squares on F
Data / restraints / parameters	11063 / 2 / 692	4285 / 0 / 212
Goodness-of-fit on F	1.020	1.035
Final R indices $[1>2\sigma(1)]$	$R_1 = 0.0488$	$R_1 = 0.0247$
	$WR_2 = 0.1160$	$WR_2 = 0.0548$
R indices (all data)	$K_1 = 0.0845$	$R_1 = 0.0367$
Lease difference in the lease	$WK_2 = 0.1438$	$WR_2 = 0.0000$
Largest diff. peak and note	0.001 and -0./// e A	1./03 and -2.211 e A
Y.		

Table 2. Bond lengths [Å] and angles [°] for **2a**.

2.2618(18) $1.758(3)$ $1.133(4)$ $1.356(8)$ $1.274(8)$ $1.154(4)$	Mn-P(3) Mn-C(7) C(1)-N(2) N(2)-C(2) C(4)-C(5) C(7)-O(7)	2.2722(17) $1.801(4)$ $1.300(5)$ $1.572(8)$ $1.390(12)$ $1.138(4)$
$\begin{array}{c} 85.30(10)\\ 178.46(14)\\ 92.17(14)\\ 91.19(12)\\ 86.94(12)\\ 92.83(10)\\ 93.21(13)\\ 95.82(5)\\ 175.5(5)\\ 115.5(5)\\ 119.5(7)\\ 178.1(3) \end{array}$	P(1)-Mn-P(2) N(1)-Mn-P(2) C(6)-Mn-C(7) P(2)-Mn-C(7) P(3)-Mn-C(7) P(2)-Mn-P(3) C(7)-Mn-P(1) C(1)-N(1)-Mn C(1)-N(2)-C(4) C(4)-N(2)-C(2) N(2)-C(4)-C(5) Mn-C(7)-O(7)	93.86(5) 89.28(9) 89.34(16) 84.21(11) 86.17(11) 170.22(4) 176.84(10) 175.6(3) 125.0(6) 117.1(6) 116.7(8) 176.8(3)
	2.2618(18) 1.758(3) 1.133(4) 1.356(8) 1.274(8) 1.154(4) 85.30(10) 178.46(14) 92.17(14) 91.19(12) 86.94(12) 92.83(10) 93.21(13) 95.82(5) 175.5(5) 119.5(7) 178.1(3)	2.2018(18) Mn-P(5) 1.758(3) Mn-C(7) 1.133(4) C(1)-N(2) 1.356(8) N(2)-C(2) 1.274(8) C(4)-C(5) 1.154(4) C(7)-O(7) 85.30(10) P(1)-Mn-P(2) 178.46(14) N(1)-Mn-P(2) 92.17(14) C(6)-Mn-C(7) 92.17(14) C(6)-Mn-C(7) 92.83(10) P(2)-Mn-C(7) 92.83(10) P(2)-Mn-P(1) 95.82(5) C(1)-N(1)-Mn 175.5(5) C(1)-N(2)-C(4) 115.5(5) C(4)-N(2)-C(2) 119.5(7) N(2)-C(4)-C(5) 178.1(3) Mn-C(7)-O(7)

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 Table 3. Bond lengths [Å] and angles [°] for 7a.

$\mathbf{P}_{\mathbf{A}} \mathbf{C}(1)$	1.017(4)	$\mathbf{P}_{\mathbf{A}} \mathbf{C}(2)$	1.003(4)
Re-C(1)	1.917(4) 1.006(4)	Re-C(2)	1.903(4)
RC-C(3) P_{Φ} N(11)	1.00(4) 2 1/2(3)	$\mathbf{R} = \mathbf{N}(21)$	2.0171(3) 2.138(3)
C(1) O(1)	2.142(3) 1 140(5)	C(2) $O(2)$	2.130(3) 1 140(5)
C(1) = O(1) C(2) = O(2)	1.140(3) 1.154(5)	C(2) = O(2)	1.149(3) 1.146(5)
C(3) = O(3) C(11) = N(12)	1.134(3) 1.204(5)	N(11) = C(11)	1.140(3) 1.476(5)
C(11) - N(12) N(12) - C(14)	1.304(5)	N(12) = C(12)	1.4/0(5)
N(12) - C(14)	1.480(5)	C(12) - C(13)	1.499(6)
C(14) - C(15A)	1.465(12)	C(14) - C(15B)	1.329(17)
N(21)-C(21)	1.148(5)	C(21) - N(22)	1.308(5)
N(22)-C(22)	1.476(5)	N(22)-C(24)	1.476(5)
C(22)-C(23)	1.500(6)	C(24) - C(25)	1.505(6)
C(1) P ₀ $C(2)$	00.23(18)	C(2) P ₂ $C(3)$	88 75(16)
C(1)-Re- $C(2)$	90.23(10) 96.16(16)	C(2)-Re- $C(3)$	02.22(15)
C(1)-Re- $C(5)$	80.10(10) 177.25(14)	C(2)-Re-N(21) C(1) De N(21)	95.52(13)
C(3)-Re-N(21)	1/7.35(14)	C(1)-Ke-N(21)	95.48(14)
C(2)-Re-N(11) C(1) D = N(11)	94.93(10)	C(3)-Ke-N(11)	94.54(14)
C(1)-Re-N(11) C(2) D = D	1/4.81(15)	N(21)-Ke- $N(11)$	83.04(12)
C(2)-Re-Br	1/0.4/(12)	U(3)-Ke-Br	94.40(11)
C(1)-Re-Br	91.57(12)	N(21)-Ke-Br	83.48(9)
N(11)-Re-Br	83.25(9)	O(1)-C(1)-Re	1/6./(4)
O(2)-C(2)-Re	1/8.4(4)	O(3)-C(3)-Re	1//.4(3)
C(11)-N(11)-Re	171.8(3)	N(11)-C(11)-N(12)	178.0(5)
C(11)-N(12)-C(12)	120.6(3)	C(11)-N(12)-C(14)	119.3(3)
C(12)-N(12)-C(14)	119.6(3)	C(21)-N(21)-Re	173.6(3)
C(21)-N(22)-C(22)	119.0(3)	N(21)-C(21)-N(22)	177.0(4)
C(22)-N(22)-C(24)	119.0(3)	C(21)-N(22)-C(24)	118.5(3)
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GRAPHICAL ABSTRACT



The preparation of diethylcyanamide and cyanoguanidine complexes of manganese and rhenium is described. The first example of bis(diethylcyanamide) complexes of these metals is also reported.

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