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Synthesis of several functionalized *cis*-diisocyanide and *fac*-triisocyanide metal complexes

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Abstract

cis-Diisocyanide metal complexes of the types *cis*-$W(CNR)_2(CO)_4$, *cis*-$ReCl(CNR)_2(CO)_3$, and $Fe(\eta^5\text{-}C_5H_5)Cl(CNR)_2$ and *fac*-triisocyanide metal complexes of the types *fac*-$W(CNR)_3(CO)_3$ and $[Fe(\eta^5\text{-}C_5H_5)(CNR)_3]Cl$ have been prepared. The isocyanides are of the type $4\text{-CNC}_6H_2\text{-3,5-}i\text{-Pr}_2\text{-f}$, whereby the functionalities f are capable of forming strong coordinative bonds to transition metals (f = CCH, $CC\text{-4-}C_5H_4N$, or $CC\text{-4,4}'\text{-biphenyl-}C_6H_2\text{-3,5-}i\text{-Pr}_2\text{-4-NC}$) or capable of being interconnected with each other by covalent bond formation (f = Br, I, CCSiMe3, CCH). The molecular structures of *cis*-$W(4\text{-CN-3,5-}i\text{-Pr}_2\text{-}C_6H_2CC\text{-4-}C_5H_4N)_2(CO)_4$, *cis*-$ReCl(4\text{-CN-3,5-}i\text{-Pr}_2\text{-}C_6H_2CCH)_2(CO)_3$, and $Fe(\eta^5\text{-}C_5H_5)Cl(4\text{-CN-3,5-}i\text{-Pr}_2\text{-}C_6H_2CC\text{-4-}C_5H_4N)_2$ have been determined by X-ray crystallography. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Isocyanides; Metal complexes; Tungsten; Rhenium; Iron; X-ray structures

1. Introduction

Isocyanide metal complexes [1] bearing donor groups in peripheral locations can undergo molecular self-assembly [2] with unsaturated metal complexes or metal ions to form coordination polymers [3,4]. Depending on the spatial arrangement of the donor groups, the isocyanide metal complexes may be designed to serve as building blocks for one-, two-, and three-dimensional solids. With square planar and octahedral building blocks, one might expect the formation of two and three-dimensional solids with open structural networks. However, open frameworks are not easily obtained by molecular self-assembly. The difficulties arise from the need to establish the intermolecular links under reversible conditions. The thermodynamically stable solid-state structures resulting from molecular self-assembly are normally space-filling [5], i.e. 'open' three-dimensional frameworks may interpenetrate and/or include solvent molecules or other guest molecules. This situation is well documented in the literature [6]. Interpenetrating three-dimensional structures are, of course, incapable of unfolding the physical properties of the individual networks, and in cases where non-interpenetrating, guest-stabilized open frameworks have been obtained, the three-dimensional frameworks often collapse upon removal of the enclosed molecules. In our own work, we have encountered a related case in a one-dimensional solid that illustrates the stereochemical 'non-rigidity' of a frequently used intermolecular link, the metal–nitrile bond [4a,c]. Thus in the construction of open three-dimensional networks by molecular self-assembly, the 'weak' directional intermolecular links are not only an essential tool in achieving spatial organization, but also the root of intrinsic difficulties. In view of this situation, we are considering an alternative approach towards the synthesis of molecular materials with zeolite-like structures that is perhaps more

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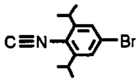
cumbersome, but ultimately more practical, namely the covalent construction of robust open molecular structures from geometrically well-defined structural subunits. Since covalent molecular structures are incapable of complete mutual interpenetration, their combination into larger assemblies or extended solids would necessarily give rise to materials with zeolite-like properties. With the rectangular geometry of isocyanide metal complex building blocks, an obvious route to robust open molecular structures could be based on the covalent linkage of square and cube corner units [7]. With this alternative strategy to open molecular structures in mind, we have synthesized several *cis*-diisocyanide and *fac*-triisocyanidemetal complexes featuring terminal functionalities capable of forming strong coordinative or covalent intermolecular bonds.

2. Experimental

The isocyanides **1**–**5** [4d,8], 2,6-diisopropyl-4-iodo-formamidobenzene [8], and 4,4′-diethynylbiphenyl [9], $W(CO)_3(NCCH_3)_3$ [10], $W(\eta^6\text{-}C_7H_8)(CO)_3$ [11], $ReCl(CO)_3(THF)_2$ [12], and $Fe(\eta^5\text{-}C_5H_5)Cl(CO)_2$ [13] were prepared as described in the literature. THF, ether, CH_2Cl_2, and *n*-hexane were distilled under N_2 from appropriate drying agents. All other solvents and reagents were of analytical grade and were used as received, unless otherwise noted. The syntheses of the transition metal complexes were performed under an atmosphere of N_2. The NMR spectra were recorded at 300 MHz for ^{1}H-NMR and 75.4 MHz for ^{13}C-NMR. The elemental analyses were performed by Butterworth Laboratories.



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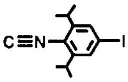

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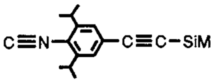

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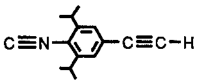

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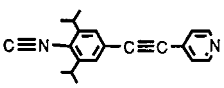
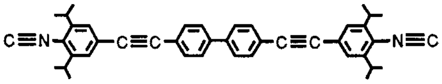


5

2.1. 4,4′-Bis(3,5-diisopropyl-4-formamidophenylethynyl)biphenyl

2,6-Diisopropyl-4-iodo-formamidobenzene (1.40 g, 4.23 mmol), copper(I) iodide (0.130 g, 0.682 mmol) and bis(triphenylphosphine)palladium dichloride (0.208 g, 0.296 mmol) are added to a flask. Then, THF (20 ml), triethylamine (80 ml), and 4,4′-diethynylbiphenyl (0.432g, 2.14 mmol) are added. The mixture is stirred at 60–70°C for 17 h. After the reaction is complete (monitored by TLC), the resulting mixture is filtered through a plug of silica gel and washed with dichloromethane. The combined filtrates are washed with water and dried over magnesium sulfate. After evaporation of the solvent, the product is obtained as a pale yellow solid, which is recrystallized from *n*-hexane (1.158 g, 89%). ^{1}H-NMR ($CDCl_3$), several isomers: δ 8.50 (s, 1 H), 8.06-8.02 (d, 1 H), 7.64–7.62 (2 d, 8 H, C_6H_4), 7.39 (s, 4 H, C_6H_2), 6.88–6.83 (d, 1 H), 6.71 (s, 1 H), 3.23–3.09 (m, 4 H, $J = 6.8$ Hz, CH); 1.26–1.24 (d, 24 H, $J = 6.8$ Hz, CH_3). ^{13}C-NMR ($CDCl_3$), several isomers: δ 164.7, 160.3 (NHCHO), 147.0, 146.6, 140.3, 140.2, 140.1, 140.0, 139.1, 132.2, 132.2, 130.6, 130.1, 130.1, 129.9, 127.4, 127.1, 127.0, 126.9, 123.9, 123.8, 123.7, 123.7, 122.6, 122.6, 122.4, 122.3, 90.6, 90.5, 90.1, 90.1, 89.7, 89.7, 89.2, 89.2(–CC–), 28.9, 28.5 (CH), 23.5, 23.5 (CH_3). IR (CH_2Cl_2, cm^{-1}): ν(NHCHO) = 1697. MS (*m*/*z*, rel. int.): 608 (35%, M).

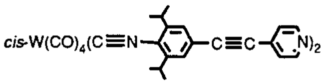
2.2. 4,4′-Bis(3,5-diisopropyl-4-isocyano-phenylethynyl)biphenyl (6)



6

Triphosgene (0.300 g/10 ml THF) is added slowly to a frozen THF solution of 4,4′-bis(3,5-diisopropyl-4-formamidophenylethynyl)biphenyl (0.60 g, 0.987 mmol) and triethylamine (0.85 ml) at −198°C. The mixture is slowly warmed to room temperature (r.t.) and stirred for 11 h. Then an aqueous solution of sodium carbonate (10%, 40 ml) is added, and the mixture is stirred for another hour. The THF is removed under reduced pressure. After adding more water, the resulting mixture is extracted with dichloromethane. The organic layer is washed with water and dried over magnesium sulfate. After evaporation of the solvent, the product is obtained as a light yellow solid (0.495 g, 87.7%). ^{1}H-NMR ($CDCl_3$): δ 7.65–7.64 (s, 8 H, C_6H_4), 7.35 (s, 4 H, C_6H_2), 3.41–3.36 (m, 4 H, CH), 1.33–1.30 (d, 24 H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 170.0 (CN), 145.3, 140.3, 132.2, 127.0, 126.7, 124.3, 122.2, 90.8 (–CC–), 89.9 (–CC–), 29.8 (CH), 22.5 (CH_3). IR (CH_2Cl_2, cm^{-1}): ν(CN) = 2118. MS (m/z, rel. int.): 573 (M + 1, 70%).

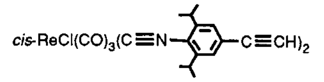
2.3. *cis-W(4-CN-3,5-i-Pr_2–C_6H_2CC-4-C_5H_4N)$_2$(CO)$_4$ (7)*



7

$W(CO)_3(NCCH_3)_3$ (55.0 mg, 0.138 mmol) is added to a solution of **5** (70.0 mg, 0.243 mmol) in THF (7 ml). The solution is stirred at r.t. for about 18 h. During this time the orange solution changes to red brown. Then THF is removed under reduced pressure. The solid residue is purified by chromotograpy on silica gel using 5:1 ethyl acetate–*n*-hexane as the eluent. The product is obtained as a brown–yellow solid (40.8 mg, yield: 38.5%). The single crystal for the X-ray crystallographic study was obtained by evaporating a solution of **7** in acetone very slowly at r.t. Found: C, 58.82; H, 4.62; N, 6.07. Calc. for $C_{44}H_{40}N_4O_4W{\cdot}1.5\ H_2O$, FW: 872.62 + 27.02 (899.65): C, 58.74; H, 4.82; N, 6.23. ^{1}H-NMR ($CDCl_3$): δ 8.63–8.61 (m, 4 H, C_5H_4N), 7.40–7.39 (m, 4 H, C_5H_4N), 7.34 (s, 4 H, C_6H_2), 3.34–3.19 (m, 4 H, J = 6.7 Hz, CH), 1.33–1.31 (d, 24 H, J = 6.9 Hz, CH_3). ^{13}C-NMR ($CDCl_3$): δ 198.7 (CO), 196.0 (CO), 147.8, 146.2, 145.6, 145.5, 144.7, 143.8, 127.6, 127.4, 127.2, 126.6, 126.2, 121.6, 87.8, 87.6, 30.2, 29.9, 29.6, 22.6, 22.5, 22.1. IR (CH_2Cl_2, cm^{-1}): ν(CN) = 2135 (m), 2073 (s); ν(CO) = 2008(s), 1940 (sh), 1929 (vs). FAB-MS (m/z, rel. int.): 873 (30%, M + 1), 845 (32%, M–CO + 1), 817 (38%, M–2CO + 1), 289 (82%, L + 1).

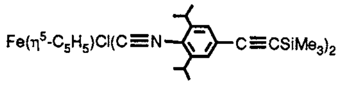
2.4. *cis-ReCl(4-CN-3,5-i-Pr_2–C_6H_2CCH)$_2$(CO)$_3$* ***(8)***



8

$ReCl(CO)_5$ (53.0 mg, 0.147 mmol) is dissolved in THF (15 ml) and refluxed for 12 h (monitored by IR). The resulting solution is then cooled to r.t., and **4** (62.0 mg, 0.294 mmol) is added. The mixture is stirred at r.t. for 24 h (monitored by IR). After removing the solvent, the solid residue is recrystallized from dichloromethane–*n*-hexane. The product is obtained as a brown–yellow solid (51.0 mg, 47.8%). Single crystals suitable for X-ray crystallography were obtained by evaporating a solution of **8** in CH_2Cl_2 slowly at r.t. Found: C, 54.97; H, 5.08, N, 3.58%. Calc. for $C_{33}H_{34}N_2O_3ReCl{\cdot}0{\cdot}2\ C_6H_{14}$, FW: 728.27 + 17.23 (745.50): C, 55.10; H, 4.98; N, 3.76. ^{1}H-NMR ($CDCl_3$): δ 7.32 (s, 4 H, C_6H_2), 3.38–3.28 (m, 4 H, J = 6.8 Hz, CH), 3.21 (s, 2 H, CC–H), 1.30–1.28 (d, 24 H, CH_3). ^{13}CNMR ($CDCl_3$): δ 186.5 (CO), 183.8 (CO), 150.4, 146.1, 127.5, 124.0, 82.8, 79.6, 30.0, 22.3. IR (CH_2Cl_2, cm–1): ν(CC–H) = 3298 (m); ν(CN) = 2179 (vw), 2146 (w); ν(CO) = 2039 (vs), 1992 (s), 1931 (s). FAB-MS (m/z, rel. int.): 729 (10%, M + 1), 694 (85%, M–Cl + 1), 673 (100%, M–2CO + 1).

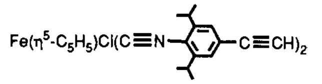
2.5. *Fe(η^5-C_5H_5)Cl(4-CN-3,5-i-Pr_2–C_6H_2CCSiMe$_3$)$_2$ (9)*



9

A solution of **3** (102 mg, 0.36 mmol) and Fe(η^5-C_5H_5)Cl$(CO)_2$ (37 mg, 0.187 mmol) in THF (8 ml) is stirred at r.t. for 40 h. The color of the solution changed to brown. When the reaction is complete (monitored by IR), the solvent is removed under reduced pressure. The solid residue is recrystallized from dichloromethane–*n*-hexane. Two components are obtained: A brown solid, **9**, (20 mg, yield: 15%) and a pale yellow solid, **18**, (33 mg, yield: 26%), which is the less soluble product. **9**: Found: C, 67.72; H, 7.61; N, 3.91%. Calc. for $C_{41}H_{55}N_2Si_2FeCl$, FW: 723.32: C, 68.08; H, 7.66; N, 3.87%. ^{1}H-NMR ($CDCl_3$): δ 7.26 (s, 4 H, C_6H_2), 4.76 (s, 5 H, C_5H_5), 3.50–3.40 (m, 4 H, J = 6.8 Hz, CH), 1.28–1.25 (d, 24 H, J = 6.9 Hz, CH_3), 0.28 (s, 18 H, $SiMe_3$). ^{13}C-NMR ($CDCl_3$): δ 181.4 (CN), 144.9, 127.3, 127.1, 122.4, 104.8, 95.7, 81.1, 29.8, 22.6, 0.1. IR (CH_2Cl_2, cm^{-1}): ν(CN) = 2120 (s), 2073 (s). FAB-MS (m/z, rel. int.): 688 (20%, M–Cl), 439 (15%, M–L), 404 (100%, M–L–Cl).

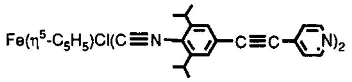
2.6. *Fe(η^5-C_5H_5)Cl(4-CN-3,5-i-Pr_2–C_6H_2CCH)$_2$* ***(10)***



10

The procedure described for **9** is followed. **4** (194 mg, 0.919 mmol), Fe(η^5-C_5H_5)Cl$(CO)_2$ (90 mg, 0.424 mmol), THF (20 ml), reaction time 16 h. Two products are obtained, a red solid, **10**, (20 mg, yield: 8.2%) and a deep brown solid, **19**, (168 mg, yield: 69.5%), which is the less soluble product. These two complexes are purified by chromatography on silica gel using 2:1 ethyl acetate–*n*-hexane for **10** and methanol for **19** as the eluents. **10**: Found: C, 72.33; H, 6.59; N, 5.20%. Calc. for $C_{35}H_{39}N_2FeCl$, FW: 579.02: C, 72.63; H, 6.74; N, 4.84%. ^{1}H-NMR ($CDCl_3$): δ 7.29 (s) and 7.26 (s) (4 H, C_6H_2), 4.76 (s, 5 H, C_5H_5), 3.6–3.3 (m, 4 H, CH), 3.16 (s, 2 H, CC–H), 1.29–1.25 (d, 24 H, CH_3). ^{13}C-NMR ($CDCl_3$): δ 181.7 (CN), 145.0, 127.6, 127.3, 121.4, 83.4, 81.1, 78.4, 29.8, 22.6, 22.5. IR (CH_2Cl_2, cm^{-1}): ν(CC–H) = 3300 (m); ν(CN) = 2124 (s), 2073 (s). FAB-MS (*m*/*z*, rel. int.): 579 (20%, M$^+$), 544 (40%, M–Cl), 367 (100%, FeLCl), 332 (95%, FeL-1).

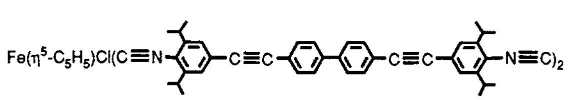
2.7. *Fe(η^5-C$_5$H$_5$)Cl(4-CN-3,5-i-Pr$_2$–C$_6$H$_2$CC-4-C$_5$H$_4$-N)$_2$* (**11**)



11

A solution of **6** (104 mg, 0.36 mmol) and Fe(η^5-C$_5$H$_5$)Cl(CO)$_2$ (38.9 mg, 0.18 mmol) in THF (25 ml) is stirred at r.t. for 36 h. After the reaction is complete (monitored by IR), the solvent is removed under reduced pressure. The solid residue is recrystallized with dichloromethane–*n*-hexane. The product is isolated as a red–brown crystalline solid (55.6 mg, yield 41.2%). Single crystals of **11** suitable for X-ray crystallography were obtained by slow evaporation of a solution of **11** in a mixture of dichloromethane and *n*-hexane. Found: C, 71.64; H, 6.41; N, 7.67%. Calc. for C$_{45}$H$_{45}$N$_4$ClFe·H$_2$O, FW: 733.13 + 18.01 (751.14): C, 71.95; H, 6.31; N, 7.46%. ^{1}H-NMR (CD$_2$Cl$_2$): δ 8.60–8.58 (m, 4 H, C$_5$H$_4$N), 7.41–7.37 (m, 8 H, C$_5$H$_4$N, C$_6$H$_2$), 4.80–4.78 (s, 5 H, C$_5$H$_5$), 3.54–3.45 (m, 4 H, *J* = 6.8 Hz, CH), 1.32–1.29 (d, 24 H, *J* = 6.8 Hz, CH$_3$). ^{13}C-NMR (CDCl$_3$): δ 182.3 (CN), 150.0,149.9, 145.3, 145.3, 131.1, 130.6, 127.4, 127.1, 125.5, 121.5, 93.6 (–CC–), 87.9 (–CC–), 81.3 (C$_5$H$_5$), 29.9 (CH), 22.6 (CH$_3$). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CN) = 2120 (s), 2071 (s). FAB-MS (*m*/*z*, rel. int.): 731 (18%, M – 1).

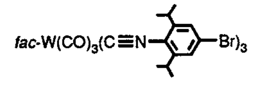
2.8. *Fe(η^5–C$_5$H$_5$)Cl(4-(4-CN-3,5-i-Pr$_2$–C$_6$H$_2$CC)–C$_6$H$_4$–C$_6$H$_4$-4′-(CCC$_6$H$_2$-2,6-i-Pr$_2$-4-NC))$_2$* (**12**)



12

This complex is prepared following the procedure described for **9**. **7** (66 mg, 0.115 mmol), Fe(η^5-C$_5$H$_5$)Cl(CO)$_2$ (9 mg, 0.042 mmol), THF (23 ml), reaction time 90 h (r.t.). The product is isolated as a yellow solid. Found: C, 74.30; H, 6.01; N, 3.53. Calc. for C$_{89}$H$_{85}$N$_4$ClFe·2CH$_2$Cl$_2$, FW:1301.89 + 169.86 (1471.75): C, 74.26; H, 6.10; N, 3.81%. ^{1}H-NMR (CD$_2$Cl$_2$): δ 7.66 (br, 16 H, C$_6$H$_4$), 7.45–7.37 (br, 8 H, C$_6$H$_2$), 4.80–4.78 (d, 5 H, C$_5$H$_5$); 3.62–3.38 (m, 8 H, CH); 1.36–1.21 (48 H, CH$_3$). ^{13}C-NMR (CDCl$_3$): δ 181.7 (NC), 146.9, 146.5, 145.2, 145.1, 140.4, 140.2, 133.1, 132.3, 132.2, 127.3, 127.0, 126.9, 126.8, 90.6, 90.3, 81.2, 80.1, 29.9 (CH), 22.7, 22.6 (CH$_3$). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CN) = 2118 (s), 2070 (s). FAB-MS (*m*/*z*, rel. int.): 1302 (M + 1), 1267 (M – Cl + 1), 729 (M–L + 1), 694 (100%, M–L–Cl + 1), 572 (L).

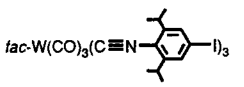
2.9. *fac-W(CN-2,6-i-Pr$_2$–C$_6$H$_2$-4-Br)$_3$(CO)$_3$* (**13**)



13

A solution of **1** (273 mg, 1.03 mmol) and W(η^6-C$_7$H$_8$)(CO)$_3$ (124 mg, 0.342 mmol) in THF (10 ml) is stirred at r.t. for 6 h (monitored by IR). The color of the solution changes to orange–yellow. The solvent is removed under reduced pressure, and the solid residue is recrystallized from *n*-hexane to afford an orange yellow crystalline solid (180 mg, yield 49%). Found: C, 48.92; H, 4.90; N, 4.15%. Calc. for C$_{42}$H$_{48}$N$_3$O$_3$Br$_3$W·1/2C$_6$H$_{14}$ FW: 1066.37 + 43.08 (1109.45): C, 48.71; H, 5.00; N, 3.79%. ^{1}H-NMR (CDCl$_3$): δ 7.25 (s, 6 H, C$_6$H$_2$), 3.34–3.24 (m, 6 H, *J* = 6.8 Hz, CH), 1.26–1.23 (d, 12 H, *J* = 6.8 Hz, CH$_3$). ^{13}C-NMR (CDCl$_3$): δ 201.4 (CO), 165.4 (CN), 146.7, 126.8, 125.3, 123.3, 122.2, 30.2, 22.3. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CN) = 2134 (w), 2058 (s); ν(CN) = 1942 (s), 1896 (s). FAB-MS (*m*/*z*, rel. int.): 1068 (1064) (100%, M + 1), 1040 (1036) (82%, (M – CO + 1).

2.10. *fac-W(CN-2,6-i-Pr$_2$–C$_6$H$_2$-4-I)$_3$(CO)$_3$* (**14**)



14

This complex is obtained following the procedure described for complex **13**. **2** (280 mg, 0.894 mmol), W(η^6-C$_7$H$_8$)(CO)$_3$ (90 mg, 0.248 mmol), THF (10 ml). Orange yellow solid (65 mg, yield: 22%). Found: C, 42.55; H, 4.01; N, 3.65%. Calc. for C$_{42}$H$_{48}$N$_3$O$_3$I$_3$W, FW: 1207.37: C, 44.78; H, 4.01; N, 3.48%. ^{1}H-NMR (CDCl$_3$): δ 7.44 (s, 6 H, C$_6$H$_2$), 3.34–3.24 (m, 2 H, CH, *J* = 6.8 Hz), 1.26–1.23 (d, 12 H, CH$_3$, *J* = 6.8 Hz). ^{13}C-NMR (CDCl$_3$): δ 201.4 (CO), 165.6 (CN), 146.7, 132.8, 126.0, 94.11, 30.1, 22.3. IR (CH$_2$Cl$_2$, cm^{-1}): ν(CN) = 2131 (vw), 2058 (s); ν(CO) = 1942 (s), 1900 (s). FAB-MS (*m*/*z*, rel. int.): 1208 (90%, M + 1).

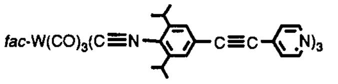
2.11. *fac-W(4-CN-3,5-i-Pr$_2$–C$_6$H$_2$CCH)$_3$(CO)$_3$* (**15**)

15

This complex is obtained following the procedure described for **13**. **4** (337 mg, 1.60 mmol), W(η^6-

$C_7H_8)(CO)_3$ (190 mg, 0.523 mmol), THF (15 ml), reaction time 13 h. The product is a deep brown solid (56 mg, yield: 11.9%). ^{1}H-NMR ($CDCl_3$): δ 7.28 (s, 6 H, C_6H_2), 3.57–3.30 (m, 6 H, CH), 3.16 (s, 3 H, CC–H), 1.29–1.23 (d, 36 H, CH_3). IR (CH_2Cl_2, cm^{-1}): ν(CC) = 3298 (m); ν(CN) = 2131 (w), 2054 (s); ν(CO) = 2009 (m), 1940 (s), 1902 (s). MS (*m*/*z*, rel. int.): 902 (45%, M + 1), 874 (65%, M–CO + 1), 816 (70%, M–3CO – 1).

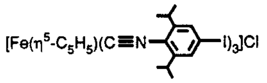
2.12. *fac*-$W(4\text{-}CN\text{-}3,5\text{-}i\text{-}Pr_2\text{–}C_6H_2CC\text{-}4\text{-}C_5H_4N)_3(CO)_3$ (**16**)



16

A solution of W(η^6-C_7H_8)$(CO)_3$ (86.0 mg, 0.237 mmol) and **6** (0.210 g, 0.729 mmol) in THF is stirred at r.t. for 48 h. After the reaction is complete (monitored by IR), the solvent is removed under reduced pressure. The solid residue is purified by chromatography on silica gel using 1:2 ethyl acetate–*n*-hexane as the eluent. Three complexes are obtained: **7** (12 mg, yield: 11.6%), **21** (72 mg, yield: 49.7%), **16** (25 mg, yield: 27.9%). **16**: Found: C, 69.35; H, 6.29; N, 6.27%. Calc. for $C_{63}H_{60}N_6O_3W{\cdot}2C_6H_{14}$, FW: 1132.98 + 172.34 (1305.32): C, 69.01; H, 6.79; N, 6.44%. ^{1}H-NMR ($CDCl_3$): δ 8.64–8.61 (m, 6 H, *J* = 4.4, 1.5 Hz, C_5H_4N), 7.42–7.31 (m, 12 H, C_5H_4N, C_6H_2), 3.43–3.28 (m, 6 H, CH), 1.32–1.23 (m, 36 H, CH_3). IR (CH_2Cl_2, cm^{-1}): ν(CC) = 2216 (vw), ν(CN) = 2129 (vw), 2118 (vw), 2052 (s), ν(CO) = 1942 (s), 1904 (s). FAB-MS (*m*/*z*, rel. int.): 1137 (M + 5).

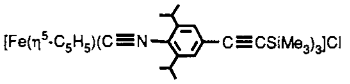
2.13. $[Fe(\eta^5\text{-}C_5H_5)(CN\text{-}2,6\text{-}i\text{-}Pr_2\text{–}C_6H_2\text{-}4\text{-}I)_3]$ Cl (**17**)



17

A solution of **2** (117 mg, 0.373 mmol) and Fe(η^5-C_5H_5)Cl$(CO)_2$ (39.7 mg, 0.187 mmol) in THF (10 ml) is stirred for 36 h under nitrogen. After removing the solvent under reduced pressure, the solid residue is recrystallized from methylene chloride–*n*-hexane. The product is obtained as a pale yellow crystalline solid (27 mg, yield: 20%). Found: C, 46.46; H, 5.11; N, 3.99%. Calc. for $C_{44}H_{53}N_3I_3FeCl{\cdot}2H_2O$, FW: 1095.89 + 36.02 (1131.91): C, 46.69; H, 5.08; N, 3.71%. ^{1}H-NMR ($CDCl_3$): δ 7.48 (s), 7.26 (s), 5.50 (s), 4.75 (s), 3.42 (br), 3.15 (br), 1.27 (s). ^{13}C-NMR ($CDCl_3$): δ 172.3 (CN), 147.0, 133.9, 126.6, 97.0, 95.0, 33.6, 26.7. IR (CH_2Cl_2, cm^{-1}): ν(CN) = 2164 (s), 2120 (s). FAB-MS (*m*/*z*, rel. int.): 1061 (100%, M–Cl + 1).

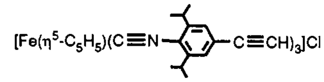
2.14. $[Fe(\eta^5\text{-}C_5H_5)(4\text{-}CN\text{-}3,5\text{-}i\text{-}Pr_2\text{–}C_6H_2CCSiMe_3)_3]$ Cl (**18**)



18

This compound was obtained as a by-product of the synthesis of **9**, as described above. Found: C, 62.39; H, 7.24; N, 3.83%. Calc. for $C_{59}H_{80}ClFeN_3Si_3{\cdot}FeCl(OH)_2$, FW: 1006.80 + 125.31 (1132.11): 62.59; H, 7.30; N, 3.71%. IR (CH_2Cl_2, cm^{-1}): ν(CN) = 2162 (m), 2116 (s). FAB-MS (*m*/*z*, rel. int.): 971 (40%, M–Cl + 1), 688 (15%, M–Cl–L + 1), 404 (100%, M–Cl–2L).

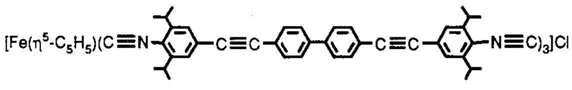
2.15. $[Fe(\eta^5\text{-}C_5H_5)(4\text{-}CN\text{-}3,5\text{-}i\text{-}Pr_2\text{–}C_6H_2CCH)_3]$ Cl (**19**)



19

This compound was obtained as a by-product of the synthesis of **10**, as described above. **19**: ^{1}H-NMR-($CDCl_3$): δ 7.29 (s, 6H, C_6H_2), 4.76 (s, H, C_5H_5), 3.23 (s, 3 H, CCH), 3.20–3.10 (m, 6 H, *J* = 6.8 Hz, CH), 1.29–1.22 (d, 36 H, *J* = 6.8 Hz, CH_3). ^{13}C-NMR ($CDCl_3$): δ 145.0, 127.7, 123.7, 84.9, 82.6, 79.9, 30.2, 22.4. IR (CH_2Cl_2, cm^{-1}): ν(CC–H) = 3298 (m); ν(CN) = 2164 (m), 2118 (s). FAB-MS (*m*/*z*, rel. int.): 755 (40%, M–Cl + 1), 544 (M–Cl–L + 1), 367 (M–2L), 332 (100%, M–Cl–2L).

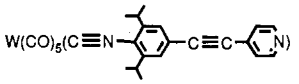
2.16. $[Fe(\eta^5\text{-}C_5H_5)(4\text{-}CN\text{-}3,5\text{-}i\text{-}Pr_2\text{–}C_6H_2CC\text{-}4\text{-}C_5H_4\text{-}N)_3]$ Cl (**20**)



20

This complex was obtained following the procedure described for **17**, using **6** (87.9 mg, 0.305 mmol) and Fe(η^5-C_5H_5)Cl$(CO)_2$ (21.6 mg, 0.102 mmol). The product is a pale yellow solid (40.7 mg, 39%). Found: C, 70.93; H, 6.24; N, 7.43. Calc. for $C_{65}H_{65}N_6ClFe{\cdot}4H_2O$. FW 1021.50 + 72.04 (1093.54: C, 71.39; H, 6.73; N, 7.69. ^{1}H-NMR ($CDCl_3$): δ 8.64 (m, 6 H, C_5H_4N); 7.40 (m, 6H, C_5H_4N), 7.36 (s, 6 H, C_6H_2); 4.80 (s, 5 H, C_5H_5); 3.53–3.48 (m, 6 H, *J* = 6.3 Hz, CH); 1.32–1.29 (d, 36 H, *J* = 6.4 Hz, CH_3). IR (CH_2Cl_2, cm^{-1}): ν(CN) = 2162 (m), 2118 (s), 2071 (w). FAB-MS (*m*/*z*, rel. int.): 986 (10%, M–Cl + 1), 409 (100%, M–Cl–2L).

2.17. $W(4\text{-}CN\text{-}3,5\text{-}i\text{-}Pr_2{-}C_6H_2CC\text{-}4\text{-}C_5H_4N)(CO)_5$ (**21**)



21

This compound was obtained as a by-product of the synthesis of complex **16**, as described above: ^{1}H-NMR ($CDCl_3$): δ 8.64–8.62 (m, 2 H, C_5H_4N), 7.41–7.39 (m, 2 H, C_5H_4N), 7.35 (s, 2 H, C_6H_2), 3.43–3.34 (m, 2 H, $J = 6.9$ Hz, CH), 1.32–1.30 (d, 12 H, $J = 6.8$ Hz, CH_3). ^{13}C-NMR ($CDCl_3$): δ 193.7 (CO), 170.7 (CN), 149.9, 145.5, 131.0, 127.3, 127.0, 125.5, 123.2, 93.1, 88.1, 29.9, 22.5. IR (CH_2Cl_2, cm^{-1}): ν(CC) = 2218 (vw), ν(CN) = 2118 (s), ν(CO) = 2054 (m), 1952 (vs). FAB-MS (m/z, rel. int.): 612 (M), 584 (M–CO), 289 (100%, L + 1).

2.18. X-ray crystallographic studies

The diffraction data for compounds **7** and **11** were collected on a Rigaku AFC7R four-circle diffractometer using X-ray radiation from a Rigaku RU-200 rotating-anode generator at 50 kV and 160 mA and processed by the MSC/Rigaku diffractometer control software. The diffraction data for compound **8** were collected on an MAR Imaging Plate Detector System using X-ray radiation from an MAR generator (sealed tube 50 kV and 50 mA), and processed by DENZO [14]. The X-ray radiation from both generators was graphite-monochromatized Mo–K_α X-ray radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections from ψ-scans were applied to the data for compounds **7** and **11**, and no absorption correction was made on compound **8**. All structure determinations and numerical calculations were done using the MSC crystal structure analysis package TEXSAN [15] using a Silicon Graphics Computer, and the full-matrix least squares refinements were on F using reflections with $I > 3\sigma(I)$. Hydrogen atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were included in the calculations, but not refined.

3. Results and discussion

The isocyanides **1**–**5** have been prepared as previously described [4d,8]. The diisocyanide **6** was synthesized by palladium-catalyzed cross-coupling [16] of 4,4′-diethynylbiphenyl with 2,6-diisopropyl-4-iodo-formamidobenzene, followed by dehydration of the formamide groups with triphosgene/triethylamine [17]. With a selection of these isocyanides, several *cis*-diisocyanide metal complexes of tungsten [18], rhenium [19],

Table 1
Crystal and data collection parameters for complexes **7**, **8**, and **11**

	7	**8**	**11**
Formula	$C_{44}H_{40}N_4O_4W$	$C_{33}H_{34}ClN_2O_3Re$	$C_{45}H_{45}ClFeN_4$
Formula weight	872.67	728.30	733.18
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)	$Pnma$ (no. 62)
a (Å)	10.908(4)	29.707(4)	11.715(3)
b (Å)	17.509(4)	10.022(2)	34.871(5)
c (Å)	21.229(6)	21.845(3)	10.016(3)
β (°)	90.26(3)	93.52(2)	90.00
V (Å^3)	4054(1)	6491(1)	4091(1)
Z	4	8	4
T (K)	301	301	301
Crystal color	Red	Yellow	Brown
Crystal dimensions (mm)	0.20 × 0.15 × 0.25	0.25 × 0.20 × 0.10	0.15 × 0.05 × 0.30
$d_{calc.}$ (g cm^{-3})	1.430	1.420	1.190
μ (cm^{-1})	28.98	38.61	4.68
Scan mode	$\omega-2\theta$		$\omega-2\theta$
$2\theta_{max}$ (°)	50.0	51.1	50.0
Unique reflections	7395	6141	4097
Reflections ($I > 3\sigma(I)$) used in LS refinement	4949	4191	1972
Number of variables	478	361	235
R	0.029[a]	0.034[a]	0.054[a]
wR	0.035[b]	0.047[b]	0.058[b]
(Δ/σ)max	0.05	0.02	0.01
Goodness-of-fit	1.38	1.69	2.23
$\Delta\rho$ (e Å^{-3})	−0.36/0.75	−1.90/0.38	−0.35/0.42

[a] $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$.

[b] $wR = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma wF_o^2]^{1/2}$, where $w = F_o^2/[\sigma^2(I) + (pF_o^2)^2]$.

Table 2
Selected bond lengths (Å) and bond angles (°)

*(a) Complex **7***			
W(1)–C(1)	2.000(6)	W(1)–C(2)	2.004(6)
W(1)–C(3)	2.026(7)	W(1)–C(4)	2.049(7)
W(1)–C(5)	2.113(5)	W(1)–C(25)	2.116(5)
N(1)–C(5)	1.153(6)	N(1)–C(6)	1.401(6)
N(2)–C(25)	1.153(6)	N(2)–C(26)	1.401(6)
C(12)–C(13)	1.167(7)	C(32)–C(33)	1.173(7)
C(1)–W(1)–C(2)	90.1(2)	C(1)–W(1)–C(25)	88.1(2)
C(2)–W(1)–C(5)	88.2(2)	C(5)–W(1)–C(25)	93.7(2)
W(1)–C(5)–N(1)	175.3(4)	W(1)–C(25)–N(2)	172.9(5)
C(5)–N(1)–C(6)	174.2(5)	C(25)–N(2)–C(26)	172.9(5)
*(b) Complex **8***			
Re(1)–Cl(1)	2.479(2)	Re(1)–C(1)	1.973(6)
Rel)–C(2)	1.977(5)	Re(1)–C(3)	2.049(7)
Re(1)–C(4)	2.092(5)	Re(1)–Cl(19)	2.079(5)
N(1)–C(4)	1.146(6)	N(1)–C(5)	1.391(6)
N(2)–C(19)	1.145(5)	N(2)–C(20)	1.397(6)
C(11)–C(12)	1.163(9)	C(26)–C(27)	1.181(7)
C(1)–Re(1)–C(2)	91.2(2)	C(1)–Re(1)–C(19)	90.4(2)
C(2)–Re(1)–C(4)	92.6(2)	C(4)–Re(1)–C(19)	86.90(2)
Re(1)–C(4)–N(1)	174.3(4)	Re(1)–C(19)–N(2)	177.5(4)
C(4)–N(1)–C(5)	173.2(5)	C(19)–N(2)–C(20)	176.9(5)
*(c) Compound **11***			
Fe(1)–Cl(1)	2.303(2)	Fe(1)–C(1)	2.109(8)
Fe(1)–C(2)	2.101(5)	Fe(1)–C(3)	2.069(5)
Fe(1)–C(4)	1.817(5)	N(1)–C(4)	1.157(6)
N(1)–C(5)	1.395(6)	C(17)–C(18)	1.183(7)
Cl(1)–Fe(1)–C(4)	89.9(3)	C(4)–Fe(1)–C(4*)	94.9(3)
Fe(1)–C(4)–N(1)	176.9(4)	C(4)–N(1)–C(5)	174.6(5)

and iron [20] have been prepared. The *cis*-diisocyanide(tetracarbonyl)tungsten complex **7** was obtained in 38% yield as the major product in the reaction of a 1:2 mixture of $W(CO)_3(NCMe)_3$ and **5** in THF. Evidently, some decomposition of $W(CO)_3(NCMe)_3$ occurred during the reaction, providing a source of carbon monoxide for the formation of the tetracarbonyltungsten fragment. The presence of $W(CO)_4(NCMe)_2$ as an impurity in $W(CO)_3(NCMe)_3$ may also have contributed to the formation of **7**. Pure **7** was isolated after chromatography on silica gel. The rhenium diisocyanide complex **8** formed in 47% yield by reaction of $ReCl(CO)_3(THF)_2$ with isocyanide **4**. The iron complexes **9**–**12** were obtained in low to moderate yield by reaction of $Fe(\eta^5\text{-}C_5H_5)Cl(CO)_2$ with two equivalents of the respective isocyanides **3**–**6**. In the syntheses of the complexes **9**–**11**, the cationic triisocyanide iron complexes [20] **18**–**20** were obtained as significant by-products. Owing to the large difference in solubility between the neutral and cationic iron complexes in organic solvents of low polarity, the neutral complexes **9**–**11** were easily separated from the cationic complexes **18**–**20** by recrystallization. Complexes **19** and **20** are formulated as the chloride salts, while complex **18** is tentatively formulated, based on elemental analysis, as an adduct with '$FeCl(OH)_2$'. Similarly the cationic triisocyanide iron complex **17** was obtained in low yield by reaction of $Fe(\eta^5\text{-}C_5H_5)Cl(CO)_2$ with two equivalents of **2**. In this case, the diisocyanide iron complex was not isolated. The triisocyanide tungsten complexes [18] **13**–**16** were obtained in low to moderate yield by reaction of $W(\eta^6\text{-}C_7H_8)(CO)_3$ with the respective isocyanides **1**, **2**, **4**, and **5** in THF, followed by chromatography on silica gel. In the reaction of $W(\eta^6\text{-}C_7H_8)(CO)_3$ with three equivalents of **5**, not only the triisocyanide tungsten complex **16** formed, but also the diisocyanide complex **7** and the monoisocyanide tungsten complex [18] **21**.

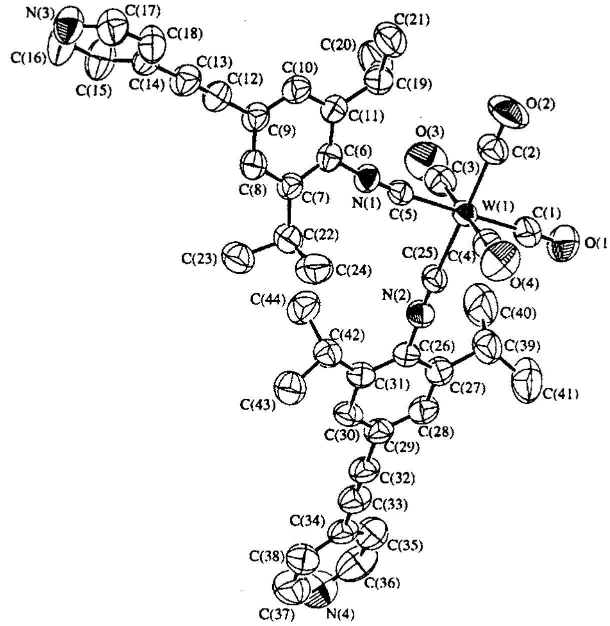


Fig. 1. Molecular structure of compound **7**. The thermal ellipsoids are shown at the 50% probability level.

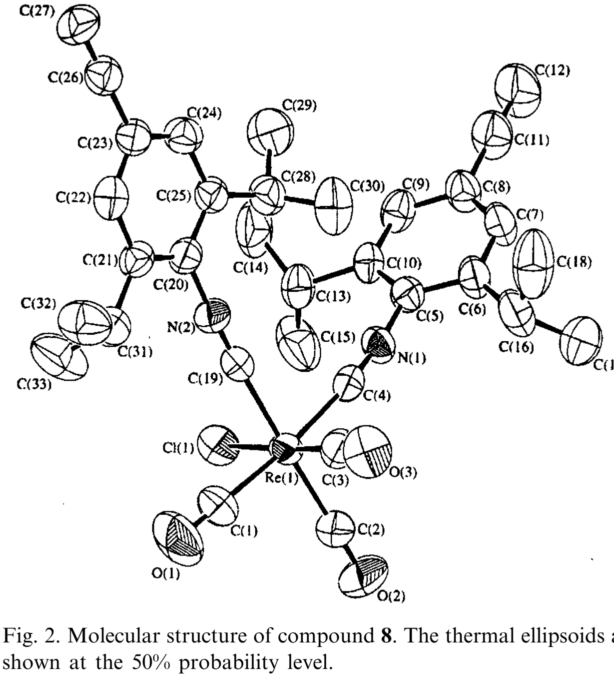


Fig. 2. Molecular structure of compound **8**. The thermal ellipsoids are shown at the 50% probability level.

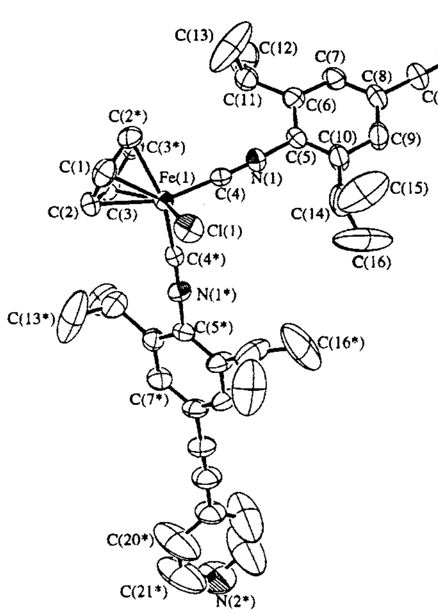


Fig. 3. Molecular structure of compound **11**. The thermal ellipsoids are shown at the 40% probability level.

The *cis* arrangement of the two isocyanide ligands in the complexes **7**–**11** is evident from the appearance of two strong IR stretching frequencies for the CN triple bonds [1]. The facial arrangement of the three isocyanide ligands in the complexes **12**–**20** is also indicated by the observation of two absorptions, one weak and one strong. All metal complexes **7**–**20** give rise to single sets of NMR signals for the isocyanide ligands, although because of the presence of paramagnetic iron(III), no well-resolved NMR spectra were obtained for **18**. For complexes **12**–**20**, this observation is only compatible with the facial arrangement of the three isocyanide ligands.

The crystal structures of complexes **7**, **8**, and **11** have been determined by X-ray crystallography. The crystallographic information is collected in Table 1. Selected bond distances and bond angles are listed in Table 2. ORTEP drawings the molecular structures of **7**, **8** and **11** are shown in Figs. 1–3. The structures confirm the *cis* arrangement of the isocyanide ligands in all three structures. The intramolecular bond distances and bond angles are within the expected range [1]. It is interesting to note that the arrangements of the planes of the isocyanide arene groups (C_6H_2-*i*-Pr_2) in the molecules **7**, **8**, and **11** correspond to the three possible regular arrangements in which the arene rings are either coplanar with or orthogonal to the $M(CNR)_2$ plane. In **7**, both arene rings are almost coplanar with the $W(CNAr)_2$ plane, in **8**, one arene group is nearly coplanar with the $Re(CNAr)_2$ plane, while the other arene group adopts a roughly perpendicular orientation, and in **11**, both arene groups are oriented approximately perpendicular to the $Fe(CNAr)_2$ plane. Owing to the bulkiness of the isopropyl substituents, the coplanar-perpendicular arrangement in the rhenium complex **8** is sterically more favorable than either the coplanar-coplanar arrangement of **7** or the perpendicular–perpendicular arrangement of **11**. Correspondingly, the RNC–M–CNR bond angle in **8** (86.90(2)°) is smaller than in **7** (93.7(2)°) or **11** (94.9(3)°). The 'outward' bending of the isocyanide ligands in **7** and **11**, which is clearly visible in Figs. 1 and 3, may be attributed to the steric repulsions between the isopropyl groups of the adjacent isocyanide ligands. At the locations of the 'outer' ethynyl carbon atoms, i.e. C(13) and C(33) for **7**, C(12) and C(27) for **8**, and C(18) and C(18)* for **11**, the effects of these steric repulsions are amplified to the extent that the interligand C–C separations of these ethynyl carbon atoms differ by several Ångstroms: C(13)–C(33) in **7** is 16.2 Å, C(12)–C(27) in **8** is 12.2 Å, and C(18)–C(18)* in **11** is 14.2 Å long. Thus the comparison of the three structures reveals a great deal of intrinsic geometric flexibility in the *cis*-$L_nM(CNR)_2$ corner units owing to the combined effects of the variable RNC–M–CNR bond angle and the bending of the 'linear' extended isocyanide ligands.

The isocyanides **4**–**6** contain functional groups which are capable of forming strong coordinative bonds to transition metal centers, namely ethynyl, 4-pyridyl, and isocyanide groups. The ligands **1**–**4** may be covalently connected in coupling and cross-coupling procedures via the halo and alkynyl substituents. Transition metal complexes of these isocyanides are therefore suitable to serve as building blocks for robust large multimetallic structures. In particular, the *cis*-diisocyanide metal complexes, e.g. **6**–**7** and **9**–**12**, could form the corners of molecular squares and the *fac*-triisocyanide metal complexes, e.g. **15**–**16** and **19**–**20** could form the corners of molecular cubes [7]. Owing to the strong binding sites and the long and slender shapes of the isocyanides, two- and three-dimensional molecular structures obtained from these building blocks could be expected to be relatively rigid and open in character.

4. Supplementary material

Crystallographic data for the structure analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 114665–114667 for compounds **7**, **8**, and **11**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax. +44-1223-336033, or E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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