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Development of a T-joint for covalent molecular construction based on 2,2′-bipyridine and phenanthroline isocyanide metal complexes

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Dedicated to Professor W.P. Fehlhammer on the occasion of his 60th birthday

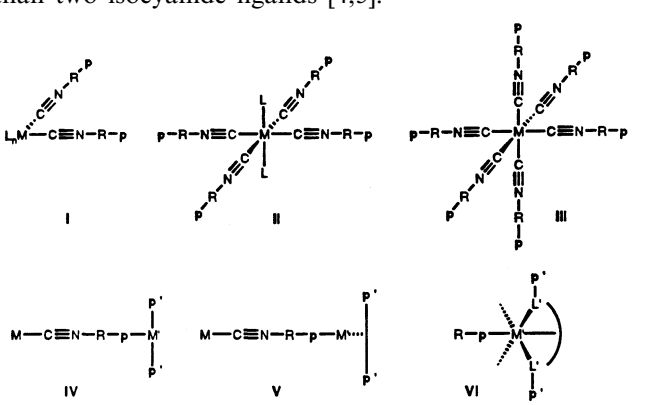
Abstract

Tetracarbonylmolybdenum and halotricarbonylrhenium complexes of laterally extendable or laterally extended bipyridines such as 5,5′-dibromo-2,2′-bipyridine, 5,5′-bis(trimethylsilylethynyl)-2,2′-bipyridine, or 3,8-dibromophenanthroline have been prepared. These complexes are potential precursors for covalent T-joints by substitution of carbon monoxide in the molybdenum complexes or halide in the rhenium complexes by linear terminal ligands. The formation of a covalent T-joint has been demonstrated by attachment of $Mo(CO)_3$(5,5′-bis(trimethylsilylethynyl)-2,2′-bipyridine) units to the free isocyanide groups of $ReCl(CO)_3$-$(CNC_6H_{10}CN)_2$. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: 2,2′-Bipyridine; Phenanthroline; Isocyanide; Metal complexes; Molybdenum; Rhenium; X-ray structure

1. Introduction

Orthogonal arrangements of linear entities provide the geometrically most transparent means of creating two- and three-dimensional objects. For this reason, transition metal complexes with rectangular arrangements of linear ligands are particularly attractive as building blocks for the design of large molecular structures. This is illustrated, for example, by the facile construction of molecular squares [1]. Molecular squares are usually made up of *cis*-configured d^8 square planar or d^6 octahedral metal complex fragments and linear ligands bearing terminal pyridyl, nitrile, or acetylide groups [2]. We have recently demonstrated that metal complexes of functionalized isocyanides can be utilized in analogous fashion [3]. Isocyanide metal complexes are furthermore particularly suitable to create little explored three-dimensional geometries on the basis of transition metal complexes containing more than two isocyanide ligands [4,5].



As one considers the geometric entities defined by various orthogonal arrangements of isocyanide ligands, e.g. **I**–**III**, it becomes apparent that their utility for molecular construction could be enhanced by establish-

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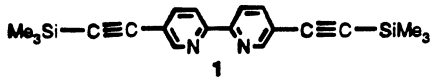
ing additional orthogonal connections at the peripheral locations **p**. Several means of achieving this are conceivable. An obvious possibility would be the attachment of suitable transition metal complex centers M′ at the locations **p**. By means of rectangular coordination geometries of M′, it would then be possible to attach linear ligands such as isocyanides to form a T-shaped connection, **IV**. Unfortunately, the selective arrangement of three linear ligands in T-shaped geometry [6] within a multimetallic structure is a difficult task. A synthetically more feasible T-joint promises to be type **V**, in which a continuous linear molecular unit is attached to M′ as a cross bar. T-joints of the general type **V** promise to be not only more facile to construct than T-joints of type **IV**, but also structurally more robust. Rigid covalent T-joints made up of laterally extended bidentate chelate ligands and linear terminal ligands can be established readily within the geometric confines of facial octahedral arrangements as indicated in **VI**. This general scheme can be implemented with many types of chelate and terminal ligands. For this initial study, 2,2′-bipyridine and phenanthroline derivatives have been chosen as the laterally extendable chelate ligands in conjunction with isocyanides as the linear terminal ligands.

2. Experimental

N-Formyl-4-bromoaniline, *N*-formyl-4-iodoaniline [7], 3,5-diisopropyl-4-formamido-ethynylbenzene [8], 5,5′-dibromo-2,2′-bipyridine [9], 3-bromophenanthroline, 3,8-dibromophenanthroline [10], *trans*-1,4-diisocyanocyclohexane [11], $[Re(SO_3CF_3)(CO)_5]$ [12], and $[ReX(CO)_3(THF)_2]$ (X = halogen) [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 used as received from commercial sources. 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 the Analytical Laboratory of Peking University and by Butterworth Laboratories Ltd.

2.1. 5,5′-Bis(trimethylsilylethynyl)-2,2′-bipyridine (*1*)

To a solution of 5,5′-dibromo-2,2′-bipyridine (700 mg, 2.2 mmol) and trimethylsilylacetylene (0.6 ml, 4.5 mmol) in triethylamine (30 ml) was added CuI (18 mg, 0.09 mmol) and $PdCl_2(Ph_3P)_2$ (66 mg, 0.09 mmol). The mixture was stirred overnight at room temperature (r.t.). The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel, using 1:6 ethyl acetate–*n*-hexane as eluant. Removal of the solvent under vacuum gave a white solid (738 mg, 96%). IR (CH_2Cl_2, cm^{-1}): 2158 (m, CC). ^{1}H-NMR ($CDCl_3$): δ 8.72 (d, 2H, H^6, $H^{6'}$); 8.36 (d, 2H, H^4, $H^{4'}$); 7.86 (q, 2H, H^3, $H^{3'}$); 0.28 (s, 18H, $SiMe_3$). ^{13}C-NMR ($CDCl_3$): δ 154.2, 152.1, 139.8, 120.5, and 120.3 (C_6H_3N), 101.7 and 99.5 (CC), −0.2 (CH_3). EI MS: 348 $[M]^+$; 333 $[M - Me]^+$.



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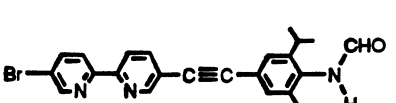
2.2. 5-(3,5-Diisopropyl-4-formamidophenylethynyl)-5′-bromo-2,2′-bipyridine (*2*) and 5,5′-bis-(3,5-diisopropyl-4-formamidophenylethynyl)-2,2′-bipyridine (*3*)

NEt_3 (40 ml) and benzene (20 ml) were added to 5,5′-dibromo-2,2′-bipyridine (0.20 g, 0.637 mmol), 3,5-diisopropyl-4-formamido-ethynylbenzene (0.33 g, 1.44 mmol), CuI (30 mg, 0.157 mmol) and $Pd(PPh_3)_2Cl_2$ (62 mg, 0.088 mmol). The mixture was stirred at 72°C for 28 h. After removal of the solvent, the residue was purified by chromatography on silica gel using 2:1–4:1 (v/v) ethyl acetate–*n*-hexane as the eluent. Two components were obtained as light yellow solids. **2**: Yield; 53 mg, 18%. IR (CH_2Cl_2, cm^{-1}): 1697 (s, NHC=O). ^{1}H-NMR ($CDCl_3$), two isomers: δ 8.82 (s, 1H); 8.74 (d, 1H, $J = 2.4$ Hz); 8.51 (d, 0.5H, $J = 1.3$ Hz); 8.41 (d, 1H, $J = 3.4$ Hz); 8.39 (d, 1H, $J = 2.8$ Hz); 8.05 (d, 0.5H, $J = 11.9$ Hz); 7.97 (d, 2H, $J = 10.0$ Hz); 7.41 (d, 2H, C_6H_2, $J = 1.3$ Hz); 6.79 (d, 0.5H, $J = 11.6$ Hz); 6.70 (s, 0.5H); 3.18 (m, 2H, CH, $J = 6.9$ Hz); 1.26 (d, 12H, CH_3, $J = 6.$ 9 Hz). ^{13}C-NMR ($CDCl_3$), two isomers: δ 164.6 and 160.3 (CHO), 154.1, 154.0, 151.7, 150.4, 147.1, 146.7, 139.6, 139.6, 139.5, 127.5, 127.2, 123.1, 122.6, 120.3, and 120.3 (phenyl and bipyridine), 93.9, 93.4, 86.7, and 86.3 (CC), 28.9 and 28.5 CH, 23.5 and 23.5 (CH_3). FAB MS: 462 $[M + 1]^+$.



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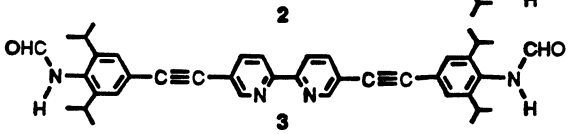

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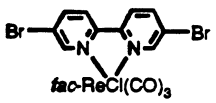
3: Yield: 105 mg, 27%. IR (CH_2Cl_2, cm^{-1}): 1697 (s, NHC=O). ^{1}H-NMR ($CDCl_3$), isomers: δ 8.43 (s, 2H); 8.51 (d, 1H, $J = 1.2$ Hz); 8.46 (dd, 2H, $J = 8.4$, $J = 3.1$ Hz); 8.05 (d, 1H, $J = 11.4$ Hz); 7.99 (m, 2H); 7.42 (s) and 7.47 (s, 4H); 6.87 (d, 1H, $J = 12.0$ Hz); 6.72 (s, 1H); 3.19 (m, 4H, CH, $J = 6.9$ Hz); 1.24 (m, 24H, CH_3, $J = 6.9$ Hz). FAB MS: 612 $[M + 2]^+$.

2.3. $ReCl(CO)_3$(5,5′-dibromo-2,2′-bipyridine) (4)

A mixture of 5,5′-dibromo-2,2′-bipyridine (370 mg, 1.18 mmol) and $ReCl(CO)_5$ (397 mg, 1.10 mmol) in 20 ml benzene was heated to 50–60°C overnight. A solid formed which was filtered off and washed several times with *n*-hexane and dried under vacuum. Yellow powder. Yield: 594 mg, 92%. IR (CH_2Cl_2, cm^{-1}): 2027 (vs, CO); 1927 (s, CO); 1904 (s, CO). ^{1}H-NMR ($CDCl_3$): δ 9.11 (d, 2H, 6,6′-bipy H's); 8.19 (dd, 2H, 4,4′-bipy H's); 8.03 (d, 2H, 3,3′-bipy H's). ^{13}C-NMR ($CDCl_3$): δ 225.9 and 206.9 (CO), 154.2, 141.8, 128.3, and 124.0 (bipyridine).



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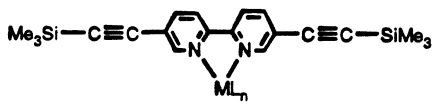
2.4. $Mo(CO)_4$(5,5′-bis(trimethylsilylethynyl)-2,2′-bipyridine) (5)

A mixture of 5,5′-bis(trimethylsilylethynyl)-2,2′-bipyridine (300 mg, 0.86 mmol) and $Mo(CO)_6$ (228 mg, 0.86 mmol) in toluene (20 ml) was refluxed overnight. The solvent was removed under vacuum. The residue was redissolved in methylene chloride, and the mixture was separated by TLC on silica gel using 1:2 (v/v) CH_2Cl_2–*n*-hexane as the eluent. A deep purple solid was obtained by removing the silica containing a purple-colored band from the plate, extraction with methylene chloride, and removal of the solvent under vacuum. Yield: 288 mg, 60%. IR (CH_2Cl_2, cm^{-1}): 2193 (w, CC); 2021 (w, CO); 1909 (vs, CO); 1882 (s, CO); 1834 (s, CO). ^{1}H-NMR ($CDCl_3$): δ 9.17 (d, 2H, 6,6′-bipy H's); 7.99 (d, 2H, 3,3′-bipy H's); 7.90 (dd, 2H, 4,4′-bipy H's); 0.31 (s, 18H, $Si(CH_3)_3$). ^{13}C-NMR ($CDCl_3$): δ 222.9 and 204.7 (CO), 155.7, 152.9, 139.8, 122.6, and 121.8 (C_5H_3N), 104.0 and 99.6 (CC), 0.37 (CH_3). Anal. Calc. for $C_{24}H_{24}O_4N_2Si_2Mo$: C, 51.80; H, 4.32; N, 5.04. Found: C, 51.50; H, 4.12; N, 5.51%. FAB MS (^{98}Mo): 530 $[M-CO]^+$.



5: ML_n = $Mo(CO)_4$
6: ML_n = *fac*-$ReCl(CO)_3$
7: ML_n = *fac*-$ReBr(CO)_3$
8: ML_n = *fac*-$Re(OTf)(CO)_3$

2.5. $ReCl(CO)_3$(5,5′-bis(trimethylsilylethynyl)-2,2′-bipyridine) (6)

A mixture of 5,5′-bis(trimethylsilylethynyl)-2,2′-bipyridine (200 mg, 0.57 mmol) and $ReCl(CO)_5$ (181 mg, 0.5 mmol) in benzene (20 ml) was stirred at 60°C overnight. After removal of the solvent, the residue was redissolved in methylene chloride and purified by TLC on silica gel using 1:2 (v/v) EtOAc–*n*-hexane as the eluent. Orange solid. Yield: 349 mg, 94%. IR (CH_2Cl_2, cm^{-1}): 2025 (vs, CO); 1923 (s, CO); 1902 (s, CO). ^{1}H-NMR ($CDCl_3$): δ 9.05 (s, 2H, 6,6′-bipy H's); 8.00 (m, 4H, 3,3′- and 4,4′-bipy H's); 0.32 (s, 18H, $Si(CH_3)_3$). ^{13}C-NMR ($CDCl_3$): δ 196.6 and 188.9 (CO), 155.7, 153.4, 141.1, 124.2, and 122.7 (C_5H_3N), 105.3 and 98.4 (CC), −0.43 (CH_3). Anal. Calc. for $C_{23}H_{24}N_2O_3Si_2ReCl$: C, 42.22; H, 3.70; N, 4.28. Found: C, 42.24; H, 3.57; N, 4.29%. FAB MS (^{187}Re): 654 $[M]^+$; 619 $[M-Cl]^+$; 598 $[M-2CO]^+$; 570 $[M-3CO]^+$.

2.6. $ReBr(CO)_3$(5,5′-bis(trimethylsilylethynyl)-2,2′-bipyridine) (7)

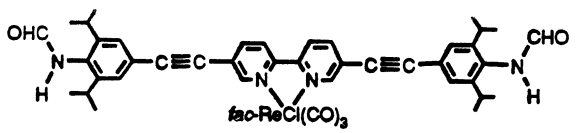
A mixture of 5,5′-bis(trimethylsilylethynyl)-2,2′-bipyridine (100 mg, 0.29 mmol) and $ReBr(CO)_5$ (77 mg, 0.19 mmol) in benzene (20 ml) was heated to 60–65°C for 4 h. After removal of the solvent, the residue was purified on silica gel using 2:1 (v/v) *n*-hexane–EtOAc as the eluent. Orange solid. Yield: 108 mg, 81%. IR (CH_2Cl_2, cm^{-1}): 2023 (vs, CO); 1925 (s, CO); 1898 (s, CO). ^{1}H-NMR ($CDCl_3$): δ 9.07 (d, 2H, 6,6′-bipy H's); 8.03 (m, 4H, 3,3′- and 4,4′-bipy H's); 0.31 (s, 18H, $Si(CH_3)_3$). ^{13}C-NMR ($CDCl_3$): δ 196.7 and 188.8 (CO), 156.3, 153.9, 141.4, 124.7, and 123.1 (C_5H_3N), 105.8 and 98.9 (CC), 0.4 (CH_3). Anal. Calc. for $C_{23}H_{24}N_2O_3Si_2ReBr$: C, 39.53; H, 3.46; N, 4.00. Found: C, 39.42; H, 3.98; N, 3.22%. FAB MS (^{187}Re): 698 $[M]^+$; 642 $[M-2CO]^+$; 619 $[M-Br]^+$.

2.7. $Re(OTf)(CO)_3$(5,5′-bis(trimethylsilylethynyl)-2,2′-bipyridine) (8)

A mixture of 5,5′-bis(trimethylsilylethynyl)-2,2′-bipyridine (108 mg, 0.31 mmol) and $Re(OTf)(CO)_5$ (147 mg, 0.31 mmol) in 20 ml benzene was heated to 50–60°C overnight. The solvent was removed under vacuum, and the residue recrystallized from CH_2Cl_2–*n*-hexane to afford a yellow powder. Based on the ^{1}H-NMR spectrum and the elemental analysis, the crystalline product contains 1 mol of water. Yield: 174 mg, 65%. IR (CH_2Cl_2, cm^{-1}): 2039 (vs, CO); 1936 (s, CO); 1919 (CO). ^{1}H-NMR ($CDCl_3$): δ 9.07 (s, 2H, 6,6′-bipy H's); 8.10 (m, 4H, 3,3′- and 5,5′-bipy H's); 1.57 (H_2O); 0.32 (s, 18H, $Si(CH_3)_3$). ^{13}C-NMR ($CDCl_3$): δ 195.0 and 190.7 (CO), 156.3, 153.7, 142.2, 124.8, and 122.6 (C_5H_3N), 106.2 and 98.0 CC, −0.5 (CH_3). Anal. Calc. for $C_{24}H_{24}O_7N_2Si_2F_3ReS\cdot H_2O$: C, 35.92; H, 3.23; N, 3.49. Found: C, 35.85; H, 3.05; N, 3.49%. FAB MS (^{187}Re): 619 $[M-OTf]^+$; 591 $[M-OTf-CO]^+$.

2.8. $ReCl(CO)_3$(5,5′(4-OHCNH-3,5-i-Pr_2-C_6H_2–CC)$_2$-2,2′-bipy) (9)

Complex **4** (200 mg, 0.32 mmol) and HCC–C_6H_2-3,5-*i*-Pr_2-4-NHCHO (151 mg, 0.66 mmol) were suspended in 40 ml of a mixture of 1:1 (v/v) triethylamine–THF. $PdCl_2(PPh_3)_2$ (36 mg, 0.05 mmol) and CuI (72 mg, 0.05 mmol) were added. The mixture was stirred at 50–60°C for 45 h. During this time, a yellow precipitate formed which was isolated by filtration. The yellow solid was washed several times with ether and methylene chloride and dried under vacuum. Yield: 220 mg, 75%. IR (CH_2Cl_2, cm^{-1}): 2178 (w, CC); 2021 (vs, CO); 1923 (s, CO); 1902 (s, CO); 1695 (s, NHCHO). ^{1}H-NMR (DMSO-d_6, two isomers): δ 9.60 (s) and 9.53 (d, J = 11.96 Hz, minor isomer, 2H, CHO) 9.12 (d, 2H, J = 1.47 Hz, 6,6′-bipy H's); 8.86 (d, 2H, J = 9.78 Hz, 3,3′-bipy H's); 8.51 (dd, 2H, J = 8.54, J = 1.95 Hz, 4,4′-bipy H's), 8.35 (s) and 7.96 (d, J = 11.47 Hz, minor isomer, 2H, NH); 7.53 (s, minor isomer) and 7.52 (s, 4H, C_6H_2), 3.29–3.05 (m, 4H, CH), 1.17 (d, 2H, CH_3). ^{13}C-NMR (DMSO-d_6): δ 232.8, 197.1, and 190.0 (CO), 160.7 (CHO), 153.5, 146.5, 141.8, 133.2, 127.2, 126.8, 124.7, 123.1, and 120.2 (phenyl and bipyridine), 97.1 and 83.8 (CC), 28.1 (CH), 23.1 (CH_3). Anal. Calc. for $C_{43}H_{42}O_5N_4ClRe$: C, 56.39; H, 4.59; N, 6.12. Found: C, 56.48; H, 5.06; N, 6.02%. FAB MS (^{187}Re): 916 $[M]^+$; 882 $[M - Cl + 1]^+$.



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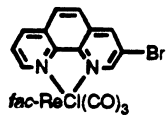
2.9. $ReCl(CO)_3$(3-bromophenanthroline) (10)

$ReCl(CO)_5$ (0.143 g, 0.395 mmol) was refluxed in THF for 14 h (monitored by IR). After cooling to r.t., 3-bromo-1,10-phenanthroline (0.1020 g, 0.395 mmol) was added. The resulting mixture was stirred at r.t. for several hours (monitored by IR). After removal of the solvent, the solid residue was recrystallized from methanol–dichloromethane. Yellow solid. Yield: 0.193 g, 87%. IR (CH_2Cl_2, cm^{-1}): 2025 (s, CO); 1925 (s, CO); 1901 (s, CO). ^{1}H-NMR ($CDCl_3$): δ 9.43 (d, 1H, J = 1.9 Hz); 9.42 (dd, 1H, J = 1.3 Hz); 8.71 (d, 1H, J = 1.9 Hz); 8.57 (dd, 1H, J = 8.2, J = 1.4 Hz); 8.07 (d, 1H, J = 8.9 Hz); 7.97 (d, 1H, J = 8.9 Hz); 7.92 (dd, 1H, J = 8.2, J = 5.1 Hz). ^{13}C-NMR (DMSO-d_6): δ 197.3, 197.0, and 189.5 (CO), 154.6, 153.8, 145.4, 144.4, 141.2, 139.4, 131.0, 130.5, 128.9, 126.8, 126.8, and 120.5 (phenanthroline). Anal. Calc. for $C_{15}H_7BrN_2O_3ClRe$: C, 31.90; H, 1.25; N, 4.96. Found: C, 31.46; H, 1.26; N, 4.94%. FAB MS (^{187}Re): 564 $[M]^+$; 529 $[M - Cl]^+$.



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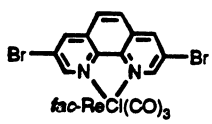
2.10. $ReCl(CO)_3$(3,8-dibromophenanthroline) (11)

This complex was obtained following the procedure described for **10**. $ReCl(CO)_5$ (0.100 g, 0.276 mmol), 3,8-dibromophenanthroline (0.092 g, 0.276 mmol). The complex is an orange–yellow solid (0.123 g, yield: 69.5%). IR (CH_2Cl_2, cm^{-1}): 2027 (s, CO); 1927 (s, CO); 1905 (s, CO). ^{1}H-NMR ($CDCl_3$): δ 9.42 (d, 2H, J = 2.01 Hz); 8.71 (d, 2H, J = 2.00 Hz); 7.99 (s, 2H). ^{13}C-NMR (DMSO-d_6): δ 196.7 and 189.1 (CO), 153.7, 144.2, 141.3, 131.1, 128.0, 120.8 (phenanthroline). Anal. Calc. for $C_{15}H_6Br_2N_2O_3ClRe$: C, 28.10; H, 0.94; N, 4.37. Found: C, 28.09; H, 1.01; N, 4.31%. FAB MS (^{79}Br^{187}Re): 642 $[M]^+$; 607 $[M - Cl]^+$.



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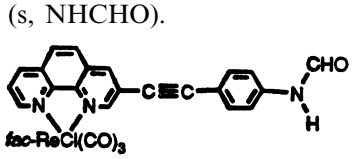
2.11. $ReCl(CO)_3$(3-(4-HOCHN–C_6H_4–CC)-phenanthroline) (12)

First, 4-formamido-trimethylsilylethynylbenzene was prepared by the reaction of 4-iodoformylaniline (5.0 g, 20.2 mmol) and trimethylsiylacetylene (3.5 ml) in the presence of CuI (0.4 g, 2.1 mmol) and $PdCl_2(PPh_3)_2$ (0.35 g, 0.5 mmol). The product is a white crystalline solid (2.97 g, yield 68%). ^{1}H-NMR ($CDCl_3$), two isomers: δ 8.72 (d, J = 11.38 Hz) and 8.40 (d, J = 1.4 Hz, 1H, CHO), 7.47 (m, 4H, C_6H_4), 7.13 (br) and 7.00 (d, J = 8.5 Hz, 1H, NH), 0.246 (s, 9H, CH_3). IR (CH_2Cl_2, cm^{-1}): 1705 (s, NHCHO). This compound was then treated with potassium hydroxide in THF to afford 4-formamido-ethynylbenzene as a white crystalline solid. ^{1}H-NMR ($CDCl_3$), two isomers: δ 8.73 (d) and 8.40 (s, 1H, CHO), 7.50 (m, 4H, C_6H_4), 7.19 (s) and 6.60 (d, 1H, NH), 3.08 (s, 1H, CCH). IR (CH_2Cl_2, cm^{-1}): 1705 (s, NHCHO).



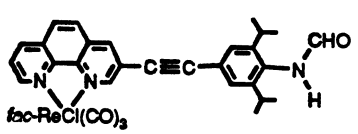
12

A flask was charged with $ReCl(CO)_3$(3-bromophenanthroline) (49.6 mg, 0.0881 mmol), HCC–C_6H_4-4-NHCHO (20.9 mg, 0.144 mmol), $PdCl_2(PPh_3)_2$ (6.3 mg,

0.009 mmol), and CuI (3.8 mg, 0.020 mmol) and THF (3 ml), DMF (3 ml), and Et_3N (4 ml) were added. The mixture was stirred at r.t. for 17 h. After removing the solvent, the solid residue was recrystallized from CH_2Cl_2 to afford a yellow solid. Yield: 46.5 mg, 83.9%. ^{1}H-NMR (DMSO-d_6, two isomers): δ 10.45 (s) and 10.39 (d); 9.44 (m); 9.14 (s); 8.97 (m); 8.32 (m); 8.12 (m); 7.72 (m). ^{13}C-NMR (DMSO-d_6, two isomers): δ 197.4, 197.1, and 189.6 (CO), 159.9 (C=O), 154.2, 153.7, 145.5, 144.4, 139.6, 133.2, 132.8, 130.8, 129.9, 128.6, 127.3, 126.7, 121.5, 119.2, 117.1, and 115.5 (phenyl and phenanthroline), 95.8 and 84.0 (CC). Anal. Calc. for $C_{24}H_{13}ClN_3O_4Re$: C, 45.82; H, 2.08; N, 6.68. Found: C, 45.82; H, 2.64; N, 6.50%. FAB MS (^{187}Re): 629 $[M]^+$; 594 $[M-Cl]^+$; 566 $[M-Cl-CO]^+$.

2.12. *ReCl(CO)$_3$(3-(4-HOCHN-3,5-i-Pr$_2$-C$_6$H$_2$–CC)-phenanthroline)* (**13**)

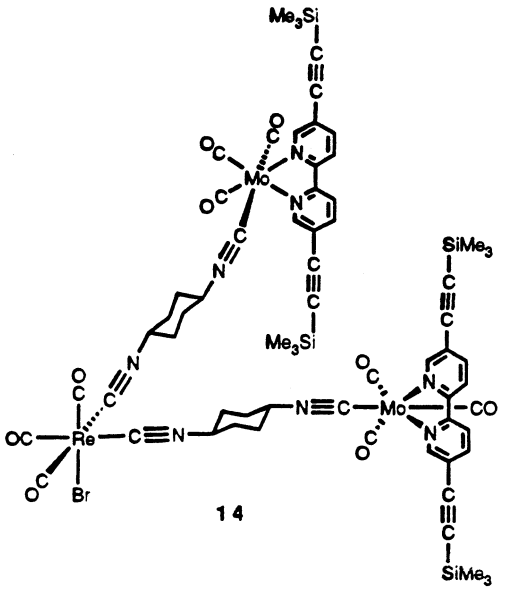
This complex was obtained following the procedure described for **12**. $ReCl(CO)_3$(3-bromo-phenanthroline) (30.0 mg, 0.053 mmol), HCC–C_6H_2-3,5-*i*-Pr_2-4-NHCHO (14.0 mg, 0.0664 mmol), $PdCl_2(PPh_3)_2$ (3.0 mg, 0.004 mmol), CuI (1.7 mg, 0.009 mmol), DMF (5 ml), Et_3N (4 ml). Yellow solid. ^{1}H-NMR ($CDCl_3$), two isomers: δ 9.47 (m); 8.66 (s); 8.55 (m); 8.06 (m); 7.94 (m); 7.50 (s); 6.78 (m); 3.20 (m, CH); 1.29 (d, CH_3). IR (CH_2Cl_2, cm^{-1}): 2212 (vw, CC); 2025 (s, CO); 1923 (s, CO); 1902 (s, CO); 1697 (s, NHCHO). FAB MS (^{187}Re): 714 $[M+1]^+$; 679 $[M-Cl+1]^+$; 651 $[M-Cl-CO+1]^+$.



13

2.13. *[Mo(CO)$_3$(5,5′-(Me$_3$SiCC)$_2$-2,2′-bipy)-(CN–C$_6$H$_{10}$-4-NC)]$_2$ReBr(CO)$_3$* (**14**)

$ReBr(CO)_3(THF)_2$ was prepared by refluxing a solution of $ReBr(CO)_5$ (0.20 mmol) in THF (20 ml) overnight. CN–C_6H_{10}–NC-4 (268 mg, 2.00 mmol) was added, and the mixture was stirred at r.t. for 10 min (monitored by IR). The solvent was removed under vacuum. The residue was washed with ether to remove the excess ligand. The product, $ReBr(CO)_3$(CN–C_6H_{10}-4-NC)$_2$, was obtained as a white solid. Yield: 53 mg, 43%. IR (THF, cm^{-1}): 2208 (w, Re–CN); 2183 (w, Re–CN); 2137 (w, NC); 2037 (vs, CO); 1979 (s, CO); 1925 (s, CO).



14

A solution of **5** (90 mg, 0.16 mmol) in CH_3CN (20 ml) was stirred at reflux for 5 h (monitored by IR). The solvent was removed under vacuum. THF (20 ml) and $ReBr(CO)_3$(CN–C_6H_{10}-4-NC)$_2$ (49 mg, 0.08 mmol) were added. The mixture was stirred at r.t. overnight. After removing the solvent under vacuum, the residue was extracted with methylene chloride and separated by TLC on silica gel using 1:2 (v/v) CH_2Cl_2–*n*-hexane as the eluent to afford a deep blue solid. Yield: 65 mg, 50%. IR (THF, cm^{-1}): 2206 (w, Re–CN); 2181 (w, Re–CN); 2106 (w, Mo–CN); 2035 (m, Re–CO); 1977 (m, Re–CO); 1921 (vs, Mo–CO and Re–CO); 1844 (s, Mo–CO); 1813 (s, Mo–CO). ^{1}H-NMR ($CDCl_3$): δ 9.22 (m, 4H, 6,6′-bipy H's); 7.94 (m, 4H, 3,3′-bipy H's); 7.84 (m, 4H, 4,4′-bipy H's); 4.24 (br, 2H, CH), 3.74 (br, 2H, CH); 2.15–1.76 (m, 16H, CH_2); 0.31 (s, 36H, $SiMe_3$). ^{13}C-NMR ($CDCl_3$), conformational isomers: δ 227.0 and 211.5 (Mo–CO), 186.1, 184.3, and 184.1 (Re–CO), 164.9, 154.7, 154.2, 152.6, 152.1, 152.0, 139.8, 138.6, 135.9, 121.6, 121.2, 120.5, and 120.4 (bipyridine), 102.9, 101.8, 99.6, and 99.5 (CC), 52.6 and 51.2 (CH), 26.2 and 26.0 (CH_2), -0.16 and -0.29 (CH_3). Anal. Calc. for $C_{65}H_{68}O_9N_8Si_4BrMo_2Re$: C, 46.59; H, 4.06; N, 6.69. Found: C, 46.12; H, 4.26; N, 6.13%. FAB MS (^{79}Br, ^{98}Mo, ^{187}Re): 1679 $[M+1]^+$; 1651 $[M-CO+1]^+$.

2.14. *X-ray crystallographic study*

The diffraction data for compound **4** 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 was graphite-monochromatized Mo–K_α X-ray radiation ($\lambda = 0.71073$ Å). The structure determination and numerical calculations were performed using the MSC crystal structure analysis package texsan [15] using a Silicon Graphic 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

Linearly extended 2,2′-bipyridines and phenanthrolines have been synthesized in large variety in recent years [16,17]. A particularly convenient route to such derivatives is provided by palladium-catalyzed cross-coupling between the requisite bromo-derivatives and terminal alkynes [18]. The bipyridine derivatives **1**–**3** have been prepared this way as the free ligands. Coordinated **3** has also been prepared in metal-coordinated form from **4**. The phenanthroline derivatives in complexes **12** and **13** have been generated after metal coordination of 3-bromophenanthroline [19]. The trimethylsilylethynyl and formylamino groups of complexes **5**–**9** and **12**–**13** are protected acetylide and isocyanide functionalities, which may be used in future studies to attach additional metal centers at these terminal positions.

Facial arrangements of bidentate chelate and terminal donor ligands, **VI**, are among the most readily established ligand combinations. Many transition metal complexes of type **VI** are also thermally and chemically very stable. The molybdenum and rhenium systems $Mo(CO)_3(L^2)L$ and $[Re(CO)_3(L^2)L]^+$ (L^2 = bipyridine, phenanthroline, L = monodentate ligand) [20,21] are particularly convenient to prepare from the precursor complexes $Mo(CO)_4(L^2)$ and $ReX(CO)_3(L^2)$ (X = Cl, Br) [22,23]. Complexes **4**–**11** were prepared by heating the respective bipyridine or phenanthroline derivatives with $Mo(CO)_6$ or $ReX(CO)_5$ (X = Cl, Br, CF_3SO_3).

Complex **5** was chosen to demonstrate the formation of a covalent molecular T-joint. Towards this goal, complex **5** was heated to reflux in acetonitrile. After complete formation of $Mo(CO)_3$(**1**)$(NCCH_3)$, the acetonitrile solvent was removed under vacuum, and the bis-isocyanide rhenium complex $ReBr(CO)_3(CNC_6H_{10}NC)_2$ and THF were added. The free terminal isocyanide groups of $ReBr(CO)_3(CNC_6H_{10}NC)_2$ displaced the acetonitrile ligands in Mo(**1**)$(NCCH_3)(CO)_3$ to afford complex **14**.

The spectroscopic data for the complexes **4**–**13** are very similar to those of the well-established parent metal complexes. The carbonyl IR absorptions of compound **5** are nearly the same as those of Mo(2,2′-bipyridine)$(CO)_4$ [24]. The ^{13}C-NMR resonances of the carbonyl ligands reflect the local symmetry at the metal center. Complexes with symmetrical bidentate ligands, e.g. **6**, give rise to only two resonances, while complexes with unsymmetrical chelate ligands, e.g. **12**, give rise to three resonances. The IR spectra of the rhenium complexes **4** and **6**–**13** feature three carbonyl absorptions, as previously observed for bipyridine and phenanthroline complexes of the general types $ReX(CO)_3$(bipy) and $ReX(CO)_3$(phen) (X = halogen) [25]. Complex **14** exhibits two sets of absorptions for the isocyanide groups, namely two absorptions for the rhenium-coordinated isocyanide groups at 2206 and 2181 cm^{-1} [13,26], and a single absorption at 2106 cm^{-1} for the molybdenum-coordinated isocyanide groups [27]. The splitting of the IR absorptions of the rhenium isocyanide groups is consistent with a *cis* arrangement of the two isocyanide ligands.

The molecular structure of **4** has been determined by X-ray crystallography (Fig. 1). The crystallographic information is summarized in Table 1. Selected intramolecular bond distances and angles are shown in Table 2. A feature of interest in the present context is the slight bending of the bipyridine ligand. The C(5)–C(8)–C(9) and C(8)–C(9)–C(12) angles deviate by about 3° from linearity. This distortion of the bipyridine ligand is evidently induced by metal coordination. The impression of the 5,5′-dibromo-2,2′-bipyridine ligand being 'curved' around the metal center is enhanced by the slight bending of the Br(1)–C(5)–(C8) and Br(2)–C(12)–C(9) angles, also by about 3°. A slight bending of the long axis of the bipyridine molecule is not unusual. In the crystal structure of protonated bipyridine, the bipyridine molecule is bent in a similar fashion as in **4**, apparently due to the attractive interactions between the proton and the

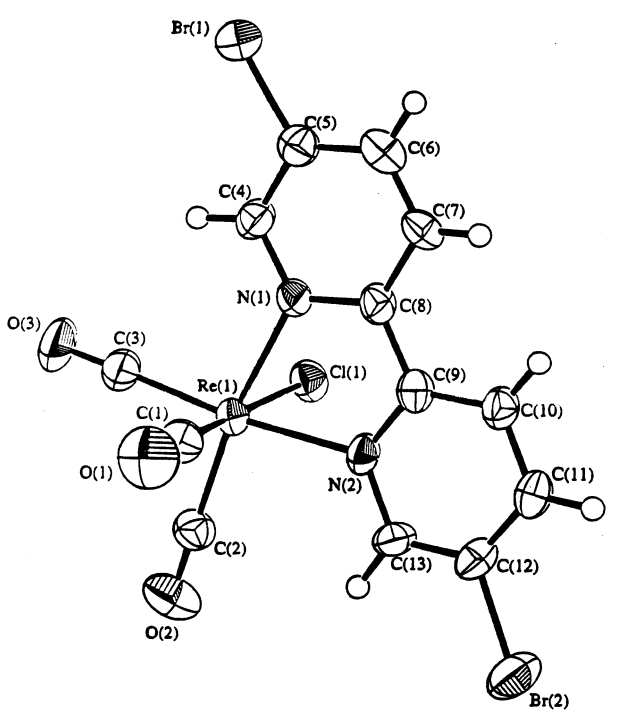


Fig. 1. Molecular structure of compound **4**. The thermal ellipsoids are shown at the 50% probability level.

Table 1
Crystal and data collection parameters for complex **4**

	4
Formula	$C_{13}H_6N_2O_3ClBr_2Re$
Formula weight	619.67
Crystal system	Triclinic
Space group	$P\bar{1}$ ($\#2$)
a (Å)	8.002(2)
b (Å)	9.484(2)
c (Å)	11.729(2)
α (°)	103.25(2)
β (°)	104.65(2)
γ (°)	97.30(2)
V (Å^3)	821.9(4)
Z	2
T (K)	301
Crystal color	Yellow
Crystal dimensions (mm^3)	$0.30\times0.15\times0.10$
μ (cm^{-1})	124.44
2θ max (°)	56.2
Unique reflections	3562
Reflections [$I>3\sigma(I)$] used in LS refinement	3206
No. of variables	199
R [a]	0.042
R_w [b]	0.057
(Δ/σ)max	0.03
Goodness-of-fit	1.52
$\Delta\rho$ (e Å^{-3})	−3.30/0.81

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

two nitrogen atoms [28]. Even in the crystal structure of 5,5′-dibromo-2,2′-bipyridine, the centrosymmetric bipyridine molecule is slightly distorted [29]. The axes defined by the carbon atoms in the 2- and 5-positions of the two pyridine rings are parallel, but not co-linear, making the molecule appear slightly twisted.

With the synthesis of complex **14**, we have accomplished the formation of stable T-joints between laterally extended bipyridine and terminal isocyanide ligands. Complex **14** demonstrates in simple fashion how a stable molecular T-joint can be used for molecular construction. The two linear bipyridine groups of **14** are fixed in space at a distance defined by the separation of the two molybdenum atoms. The bipyridine groups are perpendicular to the axes defined by the isocyanide ligands at the respective molybdenum atoms, but at the same time free to rotate about these axes. In the particular case of the 1,4-diisocyanocyclohexane bridge, several conformations of the cyclohexane ring are possible [30]. In the two major conformations with equatorial–equatorial and axial–axial positions of the isocyanide functionalities, the C–N vectors are oriented in parallel fashion and thus maintain the intended orthogonal arrangement of the chelate and isocyanide ligands. Since complex **14** is made up entirely of covalent bonds, it is a thermally as well as chemically robust molecular construct and amenable to selective transformations of the terminal functionalities of the laterally extended bipyridine ligands. Depending on the nature of the molecular fragments added to these terminal functionalities, the spatially pre-organized linear molecular units can thus be used as a framework for the covalent assembly of large well-defined molecular shapes. Transposition of this simple scheme to square planar or octahedral arrangements of four and six isocyanide ligands around a central metal atom will bring covalent three-dimensional structures of very large size and high symmetry within easy reach.

Table 2
Selected bond lengths (Å) and bond angles (°) for complex **4**

Re(1)–Cl(1)	2.485(2)	Re(1)–C(1)	1.916(9)
Re(1)–C(2)	1.926(7)	Re(1)–C(3)	1.950(7)
Re(1)–N(1)	2.172(5)	Re(1)–N(2)	2.177(5)
Br(1)–C(5)	1.881(7)	Br(2)–C(12)	1.891(7)
Cl(1)–Re(1)–C(1)	175.9(2)	Cl(1)–Re(1)–C(2)	92.8(2)
Cl(1)–Re(1)–C(3)	94.9(2)	Cl(1)–Re(1)–N(1)	83.5(2)
Cl(1)–Re(1)–N(2)	84.0(2)	N(1)–Re(1)–N(2)	74.5(2)
Br(1)–C(5)–C(4)	119.3(5)	Br(1)–C(5)–C(6)	121.4(6)

4. Supplementary material

Crystallographic data for the structural analysis of **9** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 133559. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Rd, 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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