Hydrocarbon-Bridged Metal Complexes, Part XLVI[+]

Coordination Chemistry of Pentacarbonylrheniumacetylide Complexes with Copper, Silver, and Gold(I): $(OC)_5ReC{\equiv}CRe(CO)_5$ as Ligand

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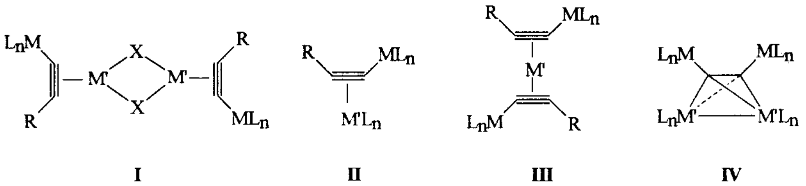
Dedicated to Professor Reinhard Nast

Abstract: The dirhenioethyne $(OC)_5ReC{\equiv}CRe(CO)_5$ (**1**) behaves as an η^2-ligand towards Cu^I, Ag^I, and Au^I in a similar way to organic alkynes or monometalated alkynes $L_nMC{\equiv}CR$. Compound **1** reacts with CuCl to give $[\{(\eta^2\text{-}\mathbf{1})Cu(\mu\text{-}Cl)\}_2]$ (**3**). Reactions of $[Cu(NCMe)_4]PF_6$, $[Ag(NCMe)_4]BF_4$, $AgSbF_6$, and AgO_2SOCF_3 with **1** and $(OC)_5ReC{\equiv}CSiMe_3$ (**2**) gave the cationic bis(alkyne) complexes $[(\eta^2\text{-}\mathbf{1})_2M]^+$ (**4**, **6**, **7**, **8**) and $[(\eta^2\text{-}\mathbf{2})_2Cu]^+$ (**10**) and the cationic dimetallic tetrahedrane $[(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathbf{1})Cu_2(NCMe)_4]^{2+}$ (**5**). The gold complexes $[(\eta^2\text{-}\mathbf{1})AuPPh_3]SbF_6$ (**11**) and $[(\eta^2\text{-}\mathbf{1})_2Au]SbF_6$ (**12**) form an equilibrium in solution. Hydrolysis of $[(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathbf{1})Cu_2(NCMe)_4](PF_6)_2$ or treatment of **2** with $[Cu(MeCN)_4]PF_6$ in moist CH_2Cl_2 afforded the difluorphosphate-bridged complexes $[\{\mu\text{-}\eta^2{:}\eta^2\text{-}[(OC)_5ReC{\equiv}CR]\}_2Cu_4(\mu_2\text{-}O_2PF_2)_4]$ (**13**: $R = Re(CO)_5$; **14**: $R = SiMe_3$). The compounds **4**, **5**, **7**, **13** and **14** were characterized by X-ray structure analysis. The stability of these complexes increases with the metal $Ag < Au \ll Cu$ and the ligand **2** < **1**.

Keywords: acetylide complexes · clusters · copper · gold · rhenium · silver

Introduction



Scheme 1. Coordination chemistry of organometallic substituted alkyne complexes $L_nMC{\equiv}CR$.

Organometallic substitued alkynes $L_nMC{\equiv}CR$[1] exhibit a rich coordination chemistry with copper(I), silver(I), and gold(I) ions,[2–6] forming complexes of the types **I**–**III** (Scheme 1; M′ = Cu^I, Ag^I, and Au^I). This versatile and structurally interesting field was comprehensively reviewed by Lang et al.[7]

In the following we report on the capability of the pentacarbonylrhenium alkynes $(OC)_5ReC{\equiv}CR$ (R = $Re(CO)_5$ (**1**), $SiMe_3$ (**2**))[8] to act as η^2-ligands in Group 11 metal complexes. We were especially interested in the coordination mode of the dirhenioacetylide $(OC)_5ReC{\equiv}CRe(CO)_5$.[9] In a series of papers it was shown[10a,b] that the $Re(CO)_5$ group which in many cases is stable towards CO substitution behaves like an isolobal[11] hydrogen atom or alkyl group. Indeed, the observed C≡C bond lengths[9b,10a] and theoretical calculations for $(OC)_5ReC{\equiv}CRe(CO)_5$ by Trogler et al.[9b] and for complexes $L_nMC{\equiv}CML_n$ of late transition metals by Sgamellotti et al.[10d] indicate that there is little change in the C≡C bond on substitution of an organic substituent by an isolobal metal fragment and that the acetylenic structure MC≡CM dominates. Bimetallic acetylide-bridged complexes were shown to be suitable building blocks for the synthesis of metal clusters[10c,12] quite similarly as organic alkynes[13] and monometallated alkynes.[10c,14]

Experimental Section

Spectroscopy and analyses: ^1H, ^{13}C, ^{13}P, and ^{19}F NMR: Jeol FX90, GSX270 and EX400. Chemical shifts are given relative to solvent peaks or TMS except ^{13}P shifts which were referenced to an external standard solution of 85 % H_3PO_4. Low-temperature measurements were always conducted on a GSX400 spectrometer. Microanalyses: Heraeus VT. IR: Perkin-Elmer

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Model 841 and Nicolet ZDX 5 FT-IR (4000-200 cm^{-1}). Finnigan MAT 90 was used for mass spectra (FAB MS: 3-nitrobenzyl alcohol as matrix and argon as exciting gas). The solvent was subtracted from the IR spectra measured in solution. Owing to the thermal instability and the tendency to decompose of the compounds, the elemental analysis and melting points of some compounds are not included in this paper.

Materials and methods: All reactions were carried out under dry high purity argon by using standard Schlenk techniques. Solvents were dried and distilled before use. Teflon or steel tubes were used to transfer dried solvents and air-sensitive solutions. Compounds $[Cu(NCCH_3)_4]PF_6$,[15] $[Ag(NCCH_3)_4]BF_4$,[16] Ph_3PAuCl,[17] Me_2SAuCl,[18] $(OC)_5ReC\equiv CRe(CO)_5$ (**1**),[9] and $(OC)_5ReC\equiv CSiMe_3$ (**2**)[8] were prepared according to slightly modified literature procedures. Other compounds were used as purchased. Silver salts were dried in vacuo for 24 h.

Preparation of the complexes

3: CuCl (8 mg, 0.08 mmol) was added to a solution of **1** (50 mg, 0.07 mmol) in THF (20 mL). The suspension was stirred vigorously at room temperature for 2.5 h to give a red solution. The solution was filtered off and the solvent removed in vacuo. The residue was washed with diethyl ether and dried under vacuum to give **3** as a bright red powder. Yield 55 mg (94%). M.p. 118 °C (decomp). IR (KBr): $\tilde{\nu} = 2151$ m,sh, 2146 sh, 2088 m, 2045 vs,sh, 2031 vs,sh, 2010 vs,sh, 1974 vs, 1960 sh, 1912 vs,br ($C\equiv O$; $C\equiv C$) cm^{-1}; MS (CI, negative-ion mode, 200 °C): m/z: 1224–1084 $[M - Re, n(CO)]^+$ ($n = 5-10$); $C_{24}Cu_2Cl_2O_{20}Re_4$ (1551.1): calcd C 18.58; found C 18.97.

4: $[Cu(NCMe)_4]PF_6$ (27.2 mg, 0.073 mmol) was added to a solution of **1** (99 mg, 0.15 mmol) in dichloromethane (20 mL). The orange solution turned pale yellow. After the mixture had been stirred for 1 h, the solvent was removed, and the residue was washed with pentane (2 × 5 mL) to give **4** as a pale yellow powder. Yield 114 mg (100%). M.p. 103 °C (decomp); IR (nujol): $\tilde{\nu} = 2155$ m, 2148 m, 2094 m, 2085 m, 2045 vs, 2026 vs,sh, 2012 vs, 1992 vs, 1976 sh, 1925 m,br ($C\equiv O$, $C\equiv C$), 886 m, 846 vs, 835 sh (P–F) cm^{-1}; ^{13}C NMR (100.53 MHz, $[D_6]$acetone, 25 °C): $\delta = 180.2$ (s, CO_{eq}), 180.0 (s, CO_{ax}), 97 (s,br, C-ethyne); MS (FAB, positive-ion mode): m/z: 1417(56.5) $[M + H - PF_6]^+$, 1389–1053 $[M + H - nCO - PF_6]^+$ ($n = 1-12$); $C_{24}O_{20}CuF_6PRe_4$ (1561.6): calcd C 18.46, found C 18.56.

5: $[Cu(NCMe)_4]PF_6$ (82 mg, 0.22 mmol) was added to a solution of **1** (146 mg, 0.21 mmol) in dichloromethane (20 mL). The solution was stirred for 1 h, then it was evaporated to 5 mL and left to crystallize overnight. Yellow prisms of **5** were collected and washed with diethyl ether (3 mL) and pentane(8 mL). Yield (crystals) 38 mg (27%). M.p. 91 °C (decomp); IR (nujol): $\tilde{\nu} = 2160$ m, 2150 s, 2112 vw, 2090m, 2064 vs, 2045 vs,sh, 2039 vs,sh, 2021 vs, 2005 vs, 1997 vs,sh 1950 w,br, ($C\equiv O$, $C\equiv C$), 2350 vw, 2319 w, 2280 w, ($N\equiv C$), 881 w,sh, 850 vs (P–F) cm^{-1}; ^{13}C NMR (100.53 MHz, $[D_6]$acetone, −40 °C): $\delta = 178.7$ (s, CO_{eq}), 178.0 (s, CO_{ax}), 122.3 (s, CH_3CN), 107. 8 (s,br, $C\equiv$), 3.4 (s, CH_3CN); ^1H NMR (400 MHz, $[D_6]$acetone): $\delta = 2.26$ (s, CH_3CN); $C_{20}H_{12}N_4O_{10}Re_2Cu_2P_2F_{12}$ (1257.7): calcd C 19.10, H 1.0, N 4.45; found C 20.41, H 1.92, N 4.05.

6: $[Ag(NCMe)_4]BF_4$ (32 mg, 0.089 mmol) was added to a solution of **1** (120 mg, 0.177 mmol) in dichloromethane (20 mL). After the mixture had been stirred for 30 min at room temperature, the solvent was removed in vacuo, and the residue was washed with diethyl ether (5 mL) and cold pentane (2 × 5 mL) to give a light brown powder that decomposed slowly (gray-brown, Ag). Yield: 125 mg (91%). IR (KBr): $\tilde{\nu} = 2155$ w,sh, 2145 m, 2132 vw,sh, 2090 m,sh, 2042 s,sh, 2011 vs, 1970 vs 1910 m,sh,br ($C\equiv O$; $C\equiv C$), 1056 s,br, 1035 sh, 950 sh (B–F) cm^{-1}; ^{13}C NMR (67.94 MHz, CD_2Cl_2): $\delta = 177.6$ (s, CO_{eq}), 177.4 (s, CO_{ax}), 88.8 (s, C-ethyne); $C_{24}AgBF_4O_{20}Re_4$ (1547.7): calcd C 18.62, found C 18.43.

7: $AgSbF_6$ (110 mg, 0.320 mol) was added at room temperature to a solution of **1** (124.1 mg, 0.183 mmol) in THF (6 mL). After the mixture had been stirred for 2 h, the solvent was removed and the residue was dried in vacuo to give a colorless powder that decomposed slowly (brown, Ag). The powder was dissolved in dichloromethane (2 mL). Colorless crystals were separated from the solution which were suitable for X-ray diffraction (black by-products). IR (crystals in nujol): $\tilde{\nu} = 2159$ m, 2154 m, 2146 s, 2098 s, 2087 s, 2065 sh, 2045 vs, 2036 vs, 2022 vs, 2005 vs, 1993 vs, 1979 vs 1917 sh ($C\equiv O$; $C\equiv C$), 659 s, 642 w,sh (Sb–F) cm^{-1}; ^{13}C NMR (67.94 MHz) (crude product, $[D_6]$acetone): $\delta = 179.8$ (s, CO_{eq}), 179.4 (s, CO_{ax}), 98 (s,br $C\equiv$).

8: AgO_3SCF_3 (50 mg, 0.20 mmol) and **1** (66 mg, 0.10 mmol) are dried in vacuo for 30 min at 30 °C. After addition of dichloromethane (20 mL) and stirring for 2 h, a precipitate was formed which was centrifuged off from the yellow solution, washed with pentane (2 × 5 mL) and dried in vacuo. Yield 82 mg (100%). M.p. 78 °C (decomp); IR (nujol): $\tilde{\nu} = 2162$ w, 2155 m, 2093m,sh, 2057 s, 2049 s, 2031 vs, 2015 vs,br, 1825 w,br ($C\equiv O$; $C\equiv C$), 1280 s,sh, 1272 s, 1250 sh, 1229 m, 1181 m, 1149 m, 1040s, 643 s (SO, CF_3) cm^{-1}; ^{13}C NMR (100.53 MHz, $[D_6]$acetone): $\delta = 179.3$ (s, CO_{ax}), 179.3 (s, CO_{eq}), 121.2 (q, $^3J(CF) = 320$ Hz, CF_3), 84.9 (s, $C\equiv C$); ^{19}F NMR (84.29 MHz, $[D_6]$acetone): $\delta = -78$ (s, CF_3); $C_{25}AgF_3O_{23}Re_4S$ (1610.0): calcd C 18.65; found C 18.45.

9: A solution of **1** (88 mg, 0.13 mmol) in THF (20 mL) was added to AgO_3SCF_3 (66.8 mg, 0.26 mol), had been previously dried in vacuo (30 min, 50 °C), and stirred. The original orange-yellow solution became colorless and after 1 h the solvent was removed. The residue was washed with diethyl ether (2 × 5 mL) and pentane (3 × 8 mL) and dried in vacuo to give a white powder that became gray (Ag) on standing. Yield 82 mg (53%). M.p. 60 °C (decomp); IR (nujol): $\tilde{\nu} = 2154$ m,sh, 2146 m, 2088m, 2080 sh, 2060 s,sh, 2041 vs,sh, 2023 vs, 2010 vs,sh, 1993 vs, 1919 w,br ($C\equiv O$, $C\equiv C$), 1353m, 1294 s, 1239 s,sh, 1220 s,sh, 1212 vs,br, 1185 vs, 1038 s, 1026 s, 642 s, 633 s (SO, CF_3) cm^{-1}; ^{13}C NMR (100.53 MHz, $[D_6]$acetone): $\delta = 178.6$ (s, CO_{eq}), 177.8 (s, CO_{ax}), 98 (br, $C\equiv C$); (CF_3 -signal not observed); ^{19}F NMR (84.29 MHz, $[D_6]$acetone): $\delta = -75.7$, -76.57, -77.89 (s, CF_3); $C_{14}Ag_2F_6O_{16}Re_2S_2$ (1190.4): calcd C 14.13; found C 14.45.

10: Compound **2** (151.5 mg, 0.36 mmol) and $[Cu(NCMe)_4]PF_6$ (67 mg, 0.18 mmol) were dissolved in dichloromethane (10 mL). The resulting pale yellow solution was stirred for 1 h and left for 20 h at room temperature. The solvent was removed in vacuo and the residue was washed with pentane and dried in vacuo. Orange yellow oil. Yield 179 mg (95%). IR (nujol): $\tilde{\nu} = 2157$ m, 2093 sh, 2072 sh, 2036 vs, 2014 vs, 1995 vs, 1985 sh, 1933 m,br ($C\equiv O$, $C\equiv C$), 849vs,br (P–F) cm^{-1}; ^{13}C NMR (100.53 MHz, CD_2Cl_2, −40 °C): $\delta = 177.5$ (s, CO_{eq}), 177.4 (s, CO_{ax}), 125.8, 117. 5, (s,br, $C\equiv$), 0.22 (CH_3); ^1H NMR (400 MHz, −40 °C): $\delta = 0.28$ (CH_3). $C_{20}H_{18}CuF_6O_{10}PRe_2Si_2$ (1055.4): calcd C 22,75, H 1.70; found C 22.45, H 1.25.

Reaction of 2 with $AgSbF_6$: $AgSbF_6$ (22 mg, 0.06 mmol) was added to a solution of **2** (54 mg, 0.13 mmol) in dichloromethane (5 mL). The colorless solution became pale yellow. After the mixture had been stirred for 15 min at room temperature, the solvent was removed in vacuo. A pale orange oil was obtained, which was stirred with pentane (10 mL) to get a colorless powder. This complex was unstable and decomposed even at −20 °C within a few hours. IR(KBr): $\tilde{\nu} = 2151$ vw, 2133 w, 2071 sh, 2035 vs, 2002 vs, 1905 m ($C\equiv O$, $C\equiv C$) cm^{-1}

11, 12: A solution of $Au(PPh_3)SbF_6$, prepared by treating a dried mixture of $Au(PPh_3)Cl$ (72 mg, 0.15 mmol) and $AgSbF_6$ (50 mg, 0.15 mmol) with dichloromethane (10 mL) and centrifugation of the resulting suspension, was added to a solution of **1** (99.5 mg, 0.15 mmol). After the mixture had been stirred for 10 min, the solvent volume was reduced to 2 mL and the solution was kept at 5 °C for 15 h. Removal of the solvent in vacuo gave a light orange powder that decomposed on standing within a few days. IR (nujol): $\tilde{\nu} = 2156$ sh, 2146 m, 2089 m, 2035 vs, 2016 vs, 2002 vs, br ($C\equiv O$); 1920 sh,br, 1880 s, br ($C\equiv C$), 718 sh, 661 s (Sb–F) cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, −40 °C): $\delta = 7.5$ (m, Ph); ^{13}C NMR (100.53 MHz, CD_2Cl_2, −40 °C): $\delta = 178.3$(s, CO_{eq}), 178.1 (s, CO_{ax}), 133.7, 132.1, 129.2, 127.5 (Ph), 114.2 (s, br, $C\equiv$); ^{19}F NMR (83.29 MHz CD_2Cl_2, 25 °C): $\delta = -182$, -167, -160, -135, -134, -89, -67 (all broad signals); ^{31}P NMR (109.38 MHz, CD_2Cl_2, 25 °C): $\delta = 38.1$ (s, PPh_3), 39.4 (s, PPh_3); MS (FAB, *m*NBA): (**11**) m/z: 1135 $[M - SbF_6]^+$, 1107–855 $[M - SbF_6 - nCO]^+$, ($n = 1-10$), 459 $[AuPPh_3]^+$; (**12**) m/z: 1551 $[M - SbF_6]^+$, 1523–1299 $[M - SbF_6 - nCO]^+$, ($n = 1-9$), 721 $[Au(PPh_3)_2]^+$.

12 (from Me_2SAuCl): A mixture of $AgSbF_6$ (27.5 mg, 0.08 mmol) and Me_2SAuCl (23.5 mg, 0.08 mol) was dried for 1 h in vacuo, and dichloromethane (10 mL) was added. The precipitated AgCl was filtered off and a solution of **1** (107.2 mg, 0.16 mmol) was added to the colorless solution of $Me_2SAuSbF_6$. Gas evolution was observed. After the mixture had been stirred for 10 min at room temperature, the solution volume was reduced to 2 mL and the light orange product was precipated by addition of pentane (20 mL). Yield 54 mg (38%). M.p. 73 °C (decomp); IR (nujol): $\tilde{\nu} = 2157$ sh, 2154 w, 2147 m, 2098 s, 2090 s, 2065 sh, 2045vs, 2024 vs, 2007 vs, 1993 vs,sh, 1982 vs, 1917 sh (CO, $C\equiv C$), 659 s, 642 w,sh (Sb–F) cm^{-1}; ^{13}C NMR (67.94 MHz, $[D_6]$acetone): $\delta = 179.8$ (s, CO_{eq}), 179.4 (s, CO_{ax}), 116 (s,br, $C\equiv$). $C_{24}AuF_6O_{20}Re_4Sb$ (1785.8): calcd C 16.14; found C 16.06.

13: After addition of wet dichloromethane (1 mL) to a freshly prepared solution of **5** (45 mg, 0.036 mmol) in dichloromethane (8 mL), the mixture was left to stand for three days. The originally yellow solution became colorless, and the product precipitated as a white powder and as crystals. Yield 35 mg (97 %). M.p. 86 °C (decomp); IR (nujol): $\tilde{\nu} = 2154$ m, 2146 s, 2091 sh, 2067 sh, 2048 vs, 2025 vs, 2010 vs, 1984 vs, 1937 m (CO), 1735 v,br,sh (C≡C), 1321 vs, 1164 vs, 1154 vs (PO), 900 s, 890 s, 863, 858 (PF) cm^{-1}. $C_{24}Cu_4F_8O_{28}Re_4P_4$ (2011.1): calcd C 14.33; found C 13.61.

14: Compound **2** (124 mg, 0.29 mmol) and $[Cu(NCMe)_4]PF_6$ (255 mg, 0.68 mmol) were dissolved in wet dichloromethane (20 mL) under gentle warming. After several days colorless crystals separated from the colorless solution which were suitable for X-ray diffraction. M.p. 69 °C (decomp); IR (nujol): $\tilde{\nu} = 2154$ s, 2091 s, 2083 sh, 2049 vs, 2021 vs, 2003 sh, 1990 vs, 1954 m (C≡O), 1785 w, 1746 m (C≡C), 1313 vs, 1164 vs, 1155 vs (P-O), 905 s, 895 s, 864 s, 849 s (P–F) cm^{-1}. $C_{20}H_{18}Cu_4F_8O_{18}Re_2Si_2P_4$ (1505.0): calc. C 15.96, H 1.21; found C 15.88, H 1.52.

Crystal structure analyses: The molecular structures of compounds **4**, **5**, **7**, **13** and **14** were dertermined on a Syntex R3 diffractometer. All measurements were carried out at 293 K. $Mo_{K\alpha}$ radiation with a graphite monochromator was used in all cases. Data were collected with the omega scan technique. Semiempirical absorption corrections were performed by means of psi-scans for all structures. The Patterson method was used to solve the structures with SHELXTL PLUS 4.11/V. Refinements were performed with a PC version of SHELXL-93. Hydrogen positions were fixed geometrically and refined with the riding model approximation with a temperature factor fixed at 1.3 times the value of the equivalent isotropic displacement parameter of the corresponding carbon atom. In compounds **4** and **5** the fluorine atoms of the disordered PF_6 groups were refined isotropically. Additionally, C(15) of compound **5** and C(13) of compound **7** had to be refined isotropically. Details of the crystal structure analyses are given in Table 1.

Reactions of $(OC)_5ReC{\equiv}CR$ (R = $Re(CO)_5$, $SiMe_3$,) with copper(I), silver(I) and gold(I) compounds

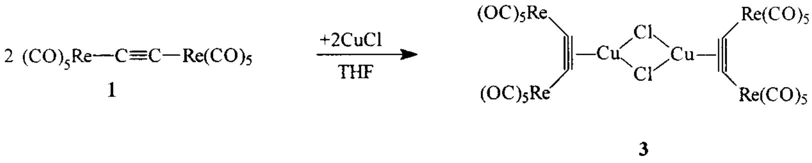
Introductory remarks: Some aspects of the chemistry of the pentacarbonylrheniumacetylides **1** and **2** have already been reported.[8, 12a] IR spectroscopy has proven to be a suitable method to monitor the course of chemical reactions involving the $(OC)_5Re$ group:[8] The ν(CO) frequencies of the products are higher than those of the starting σ-alkynyl complexes $(OC)_5ReC{\equiv}CR$, and most significantly, the a_1-CO absorption band of the $Re(CO)_5$ group appears about 15–25 cm^{-1} higher. The ν(C≡C) bands show a bathochromic shift of about 50–100 cm^{-1} upon side-on π coordination of the acetylenic triple bond. This decrease is similar to that observed upon coordination of organic alkynes to copper(I) and silver(I) salts and also in many other alkyne complexes.[19] However, due to both the presence of two $Re(CO)_5$ groups (with sometimes lower symmetry than C_{4v}) and a coordinated C≡C bond, coupling of C–O and C–C vibration modes may lead to superposition of these vibrations, making an unambiguous assignment of observed IR bands to one or the other vibration mode impossible. Also ^{13}C NMR measurements proved to be difficult for several reasons:

- long relaxation times of quaternary carbon atoms (e.g. CO, C≡C) lead in combination with coordination to large quadrupole nuclei such as Cu to weak and broad NMR absorptions
- low solubility of the obtained high-molecular-weight species.
- Many complexes establish dynamic equilibria between different species in solution, due to the high lability of alkyne ligands in complexes with the coinage metals.[19–21]

As was also observed by others before,[4a, 19, 20] despite the relatively strong influence of π coordination on the C–O (and C–C) IR absorptions, only a marginal influence on the chemical shifts of the carbonyl ligands and the acetylenic carbon atoms can be seen in the ^{13}C NMR spectra.

Results and Discussion

CuCl has been treated before with several iron, ruthenium, molybdenum and manganese acetylide complexes $L_nMC{\equiv}CR$ resulting in either monomeric[2c, 3] or dimeric chloro-bridged π complexes[2a,b, 4a]. The complex **1** reacts with a suspension of CuCl in THF to give a red solution of **3** (Scheme 2).



Scheme 2. Reaction of **1** with CuCl.

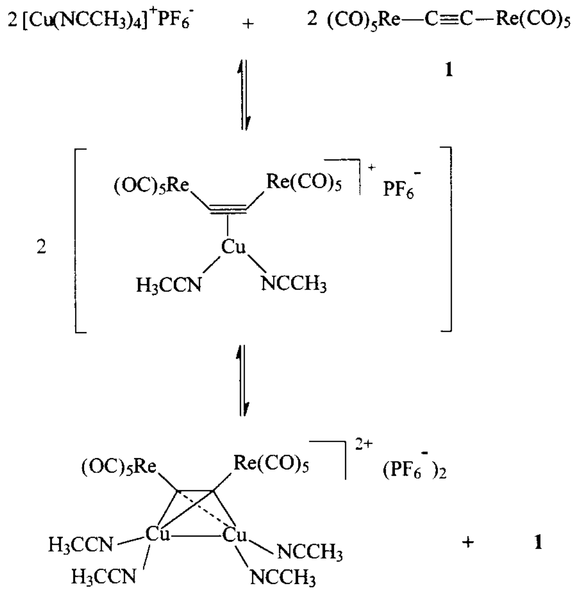
Table 1. Crystallographic data[32] for **4**, **5**, **7**, **13**, and **14**.

	4	**5**	**7**	**13**	**14**
empirical formula	$C_{24}CuF_6O_{20}PRe_4$	$C_{20}H_{12}Cu_2F_{12}N_4O_{10}P_2Re_2$	$C_{24}AgF_6O_{20}Re_4Sb$	$C_{24}Cu_4F_8O_{28}P_4Re_4$	$C_{20}H_{18}Cu_4F_8O_{18}P_4Re_2Si_2$
MW	1561.55	1257.76	1696.66	2011.08	1504.96
crystal size [mm]	0.38 × 0.17 × 0.12	0.35 × 0.1 × 0.1	0.50 × 0.30 × 0.30	0.3 × 0.24 × 0.12	0.28 × 0.09 × 0.08
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*n*
a [Å]	10.830(6)	13.598(5)	12.773(4)	9.079(6)	10.856(8)
b [Å]	15.713(6)	22.370(4)	24.148(9)	9.103(5)	10.544(6)
c [Å]	22.805(5)	11.810(7)	12.807(5)	17.469(10)	19.326(9)
β [°]	91.06(3)	97.55(4)	93.26(3)	94.78(2)	90.03(5)
V [$Å^3$]	3880.1(27)	3561.3(26)	3943.8(25)	2419.6(10)	2209.0(23)
Z	4	4	4	2	4
ρ_{calcd} [$g\,cm^{-3}$]	2.673	2.346	2.857	2.760	2.263
μ [mm^{-1}]	13.116	8.159	13.491	11.932	7.643
2θ range [°]					
4.42 →44.10	3.02 →43.12	4.38 →44.20	4.08 →44.16	4.22 →42.10	
index ranges	$+h, +k, \pm l$	$\pm h, -k, \pm l$	$\pm h, \pm k, -l$	$\pm h, +k, \pm l$	$-h, +k, \pm l$
reflections coll.	5094	8206	9978	5964	2531
indep. refl. (R_{int})	4790 (0.0635)	4119 (0.0770)	4862 0.0964)	2994 (0.0669)	2372 (0.0553)
observed ($F > 4\sigma(F)$)	3454	2947	3418	2521	1750
max./min. transm.	0.299/0.092	0.299/0.092	0.052/0.024	0.065/0.018	0.245/0.118
largest diff. hole/peak [e $Å^{-3}$]	– 1.595/1.772	– 1.215/2.793	– 1.031/1.096	– 1.220/1.038	– 2.053/2.497
$R1/wR2$ [$F > 4\sigma(F)$]	0.0518/0.1188	0.0757/0.1597	0.0497/0.1025	0.0342/ 0.0780	0.0735/0.1932
$R1/wR2$ (all data)	0.0845/0.1372	0.1089/0.1766	0.0793/0.1150	0.0443/ 0.0834	0.1013/0.2288
GoF	1.041	1.147	1.120	1.025	1.099

No signals were detected in a ^{13}C NMR spectrum run overnight. The IR spectrum of **3**, especially the shift of the a_1 CO band to 2151 cm^{-1} (from 2135 cm^{-1} in **1**) and the appearance of a very strong $\nu(\mathrm{C{\equiv}C})$ absorption band at 1912 cm^{-1}, suggests π coordination. Evidence for the dimeric structure of **3** comes from the mass spectrometric results, although the molecular ion is missing. Attempts to obtain crystals of **3** afforded the thermodynamically very stable compound $(\mathrm{OC})_5\mathrm{ReCl}$. Such a substitution of the alkynyl ligand by chloride has been observed before in reactions of manganese alkynyl complexes with AuCl(tht) or $[\mathrm{NMe_3(CH_2Ph)}]\mathrm{Cl}$.[3] To avoid this problem, metal salts with weakly coordinating anions were chosen as starting materials.[22]

Cationic Cu$^{\mathrm{I}}$ complexes, formed in situ from $[\mathrm{Cu(NCMe)_4}]^+$ and chelating nitrogen donor ligands such as tropocoronands,[23] phenanthroline[19] or bipyridine,[21b] reacted with organic alkynes to give either monomeric 1:1 complexes $[\mathrm{Cu(NN)(RC{\equiv}CR)}]^+$ or alkyne-bridged 2:1 complexes $\{[\mathrm{Cu(NN)}]_2(\mathrm{RC{\equiv}CR})\}^{2+}$, (NN = chelating nitrogen donor ligand), depending on the nature of NN and R, and to a lesser extent on the stoichiometry of the reactants. In some instances equilibria between these two types were established.[21b] The reaction of equimolar amounts of $[\mathrm{Cu(NCMe)_4}]\mathrm{PF_6}$ and **1** gives presumably first the 1:1 complex $[(\eta^2\text{-}\mathbf{1})\mathrm{Cu(NCCH_3)_2}]\mathrm{PF_6}$, which displays an IR absorption at 1930 cm^{-1} immediately after the onset of the reaction, possibly due to $\nu(\mathrm{C{\equiv}C})$ (by comparison with other alkyne-copper(I) complexes[3, 4a, 23] and the Raman absorption of **1** at 2002 cm^{-1}). This absorption gradually disappears and is replaced by new bands before a precipitate forms. This precipitate was identified by X-ray diffraction to be the tetrametallic alkyne-bridged complex **5** (Scheme 3).

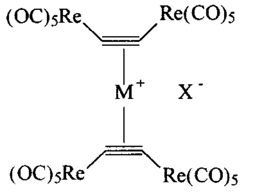
The ^{13}C NMR spectrum shows a broad absorption at δ = 107.8, which we assign to the coordinated alkyne carbon atoms. This corresponds to a low-field shift of more than 13 ppm compared to the free ligand, which is quite unusual for Cu$^{\mathrm{I}}$ complexes of organic as well as metal-organic alkynes (see above).



5

Scheme 3. Formation of the tetrametallic alkyne-bridged complex **5**.

When the same reactants are mixed in a copper/alkyne ratio of 1:2.1 in the same solvent ($\mathrm{CH_2Cl_2}$), another product **4** (Scheme 4) can be isolated after recrystallization, as evidenced by a slightly different IR spectrum and a broad ^{13}C NMR signal at δ = 97, assigned to the alkyne carbon atoms. A crystal structure determination (see below) confirmed that this compound was a copper bis(alkyne) complex. Compounds of this type were obtained by Riera et al. by treating the CuCl complex of $[\mathrm{Mn(CO)_3(dppe)(C{\equiv}CR)}]$ with $\mathrm{TlPF_6}$ in the presence of free alkynyl complex.[3] The relatively small downfield shift of the acetylenic ^{13}C resonance upon coordination is in accordance with other alkyne copper(I) complexes, which contain only one copper ion coordinated to the triple bond. From the IR data we assume that in solution there is an equilibrium between **4** and **5**, which presumably proceeds via the intermediate $[(\eta^2\text{-}\mathbf{1})\mathrm{Cu(NCCH_3)_2}]^+$.



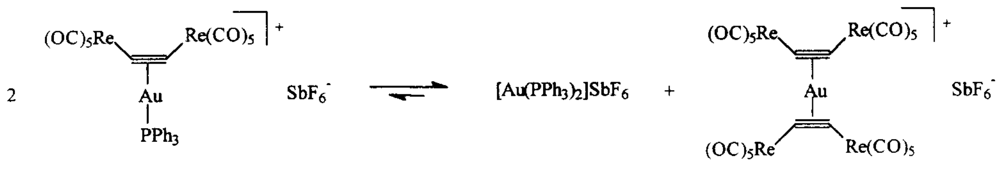
	M	X
4	Cu	$\mathrm{PF_6}$
6	Ag	$\mathrm{BF_4}$
7	Ag	$\mathrm{SbF_6}$
8	Ag	$\mathrm{CF_3SO_3}$

Scheme 4.

In comparison to the amount of research on the interactions between Cu$^{\mathrm{I}}$ and alkynes, there has been far less work on the analogous interactions with Ag$^{\mathrm{I}}$ ions. An early study by Lewandos et al. on the reaction of silver triflate with alkynes showed rapid equilibria between free and complexed alkynes.[24] NMR titrations of solutions containing alkynes with $\mathrm{AgO_3SCF_3}$ showed a maximum Ag$^+$/alkyne ratio of 1:1, and so far only silver alkyne complexes with stoichiometries 1:2 or 1:1 have been characterized.[7, 25]

When we treated **1** with 0.5 equivalents of $[\mathrm{Ag(NCMe)_4}]\mathrm{BF_4}$ or with 2.0 equivalents of $\mathrm{AgO_3SCF_3}$ in dichloromethane, two products **6** and **8** were isolated. According to their elemental analyses both these compounds exhibited 2:1 stoichiometries, similar to that for the copper complex **4**. Compounds **6** and **8** display sharp resonances in their ^{13}C NMR spectra at δ = 88.8 ($\mathrm{CD_2Cl_2}$) and δ = 84.9 ([D$_6$]acetone), respectively. We assign these signals to the acetylenic carbon atoms, which are high-field shifted from those in **1**, as observed with other alkyne silver(I) complexes.[4b, 26] The initial step of the reaction might involve the analogous silver complex $[(\eta^2\text{-}\mathbf{1})\mathrm{AgL_2}]^+$.

The reaction of **1** with 1.75 equivalents of $\mathrm{AgSbF_6}$ in THF yielded, after evaporation of the solvent, an unstable compound that displays a broad ^{13}C NMR signal at δ = 98 in acetone. The shape of this signal suggests the occurrence of equilibria in solution, which might involve a dimetallatetrahedrane $[(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathbf{1})\mathrm{Ag_2(thf)_4}]^{2+}$, analogous to **5**. However, when the crude product was recrystallized from dichloromethane, a compound was obtained that was characterized by



11 **12**

Scheme 5. Equilbrium between **11** and **12**.

X-ray diffraction to be the bis(alkyne) complex **7**. Thus it seems that in CH_2Cl_2 the low solubility of the $\{Ag[(OC)_5Re\text{-}C{\equiv}C\text{-}Re(CO)_5]_2\}^+$ complex allows its isolation, regardless of the stoichiometry of the starting materials employed.

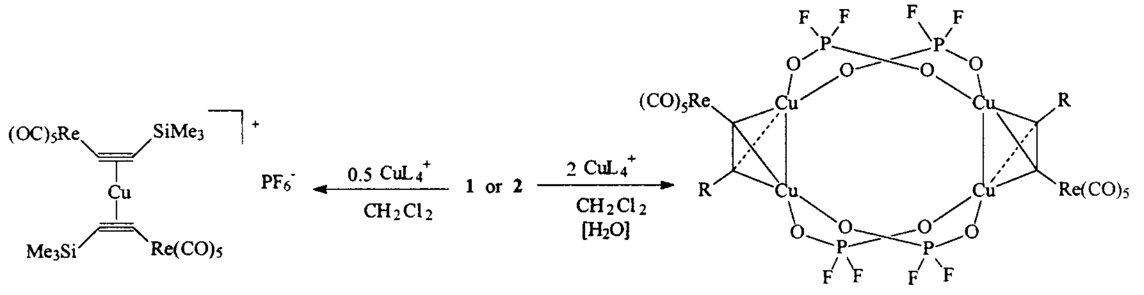
Treatment of **1** with two equivalents of AgO_3SCF_3 in THF gives, after evaporation of solvent, a product **9**, which is different from the CH_2Cl_2 reaction product **8**. The appearance of a broad ^{13}C NMR absorption at $\delta = 98$ as well as the lack of a ^{13}C NMR signal for the CF_3 group and the occurrence of three ^{19}F NMR signals suggests the presence of several species that are in rapid equilibrium. The elemental analysis is consistent with a formulation as $\mathbf{1}\cdot 2\,AgO_3SCF_3$ (**9**), a composition which corresponds to that of **13**.

Most of the silver complexes **6**–**9** decompose on standing, apparently under formation of elemental Ag, especially the products **7** and **9** from the reactions in THF. This indicates that **1** is oxidized rather giving stable π complexes. The mass spectra of the reaction products revealed a number of different complexes; the molecular ion at *m*/*z* 324 might correspond to the $[(OC)_9Re_2C_2]^{2+}$ cation which could be formed from a primary oxidation product $[(OC)_5Re{=}C{=}C{=}Re(CO)_5]^{2+}$ by CO elimination. The oxidation of polyacetylide-bridged compounds $L_nM(C{\equiv}C)_mML_n$, for example, with silver(I) ions to give highly interesting cumulenes $L_nM{=}(C{=}C)_m{=}ML_n$ has recently been a matter of extensive research.[27]

Riera et al. reported the reactions of $[Mn(CO)_3(dppe)(CCPh)]$ and gold complexes Au(L)(X) ($L = PPh_3$ or tht and $X = PF_6$), prepared in situ from the corresponding chloro complex and $TlPF_6$. With the phosphane complex, a cationic monoalkyne complex was obtained, which readily disproportionated into $[Au(PPh_3)_2]^+$ and a cationic bis(alkyne) complex, which could also be obtained directly from the tht complex and two equivalents of the manganese alkynyl complex.[3] Also when we treated **1** with one equivalent $Au(PPh_3)SbF_6$ (in fact the integrity of the anion is not sure, since the ^{19}F NMR spectrum of the product mixture showed seven broad signals, spread over 120 ppm, suggesting the presence of several species of the type X-F-(SbF_4)-F, e.g. $Sb_2F_{11}^-$), prepared in situ from the chloride and $AgSbF_6$, we obtained an equilibrium mixture of monoalkyne complex **11**, bis(alkyne) complex **12**, and $[Au(PPh_3)_2]^+$ (Scheme 5). This was confirmed by a FAB-MS spectrum, which showed the fragmentation patterns for both complexes. Independently, compound **12** was obtained from $Au(SMe_2)SbF_6$, prepared in situ from the chloride and $AgSbF_6$, and two equivalents of **1**, and was characterized by a ^{13}C NMR absorption at $\delta = 116$ (in $[D_6]$acetone) ($\delta = 117.5$ in CD_2Cl_2). The broadness of this signal suggests that **12** is prone to further equilibration reactions.

We also examined the reaction of **2** with $[Cu(NCMe)_4]PF_6$ and $AgSbF_6$, respectively. Under conditions similar to those employed for the formation of **4** a product **10** is obtained, which according to its elemental analysis is also a bis(alkyne) complex (Scheme 6). The ^{13}C NMR spectrum displays two signals in the range $\delta = 100-130$, that is at $\delta = 117.5$ and $\delta = 125.8$, which, if attributable to the alkyne carbon atoms, would imply an unusually large downfield shift for both carbon atoms in comparison to **2**, und thus indicate a dimetallatetrahedrane structure like **5**. The product derived from the analogous reaction of $AgSbF_6$ with two equivalents of **2** decomposes very fast in solution even at $-20\,^{\circ}C$ and could not be characterized.

When **2** was treated with two equivalents of $[Cu(NCMe)_4]PF_6$ in dry dichloromethane for one hour, only a mixture of several compounds, presumably containing the unconverted copper salt, is obtained. When the reaction was performed, however, in warm wet dichloromethane for several days, a crystalline compound **14** was isolated (Scheme 6), which was identified by X-ray diffraction as being composed of two dimetallatetrahedranes bridged by four difluorophosphate anions. This structure type was first obtained by Reger et al.



10

13 R = Re(CO)5
14 R = SiMe3

Scheme 6. Synthesis of **10**, and **13** and **14** from **1** or **2** and CuL_4.

from the reaction of $Cu_4(O_2CCF_3)_4 \cdot 2\,C_6H_6$ and several alkynes about ten years ago.[21a]

A similar complex **13** resulted from the deliberate hydrolysis of **5**. As could be ascertained by another X-ray structure determination, **13** is an octanuclear complex with four difluorophosphate bridges between two dimetallatetrahedrane units. The partial hydrolysis of hexafluorphosphate has been observed for a series of complexes[28] and it can be assumed that hydrolysis takes place by catalytic action of the copper ion.[29] We are particularly interested in complex **13** since it contains components of two of our major research fields: weakly coordinated anions[10b] and hydrocarbon-bridged metal complexes.[10a]

Unfortunately, NMR studies could not be conducted on **13** and **14** because of the low solubility of the complexes. In the IR spectra the $\nu(C\equiv C)$ absorptions (nujol) are shifted from 2000 (**1**, Ra) to 1735 cm^{-1} for **13**, and from 2116 (**2**) to 1746 cm^{-1} for **14**, as would be expected by comparison with other alkyne copper complexes in which the alkyne acts as a four-electron donor. This observation also shows the very different electronic effect of the anionic $PO_2F_2^-$ ligand in comparison to the neutral acetonitrile ligands in **5**, where no IR absorptions were identified in the 1800–1600 cm^{-1} range.

X-ray structure determinations of 4, 5, 7, 13, and 14

4 and **7** (Figures 1 and 2): In both complexes the two alkyne ligands lie perpendicular to each other (interplanar angle between the $MC\equiv C$ planes is 90.5° (**4**) and 89.2° (**7**)); the average Cu–C distance in **4** is 2.055(10) Å and the average Ag–C distance in **7** is 2.25 (1) Å. Thus, in both complexes the metal has a pseudo-tetrahedral environment, as might be expected for a d^{10} ion with four carbon donors. A similar arrangement of ligands was observed in the copper–manganese acetylide complex $\{Cu[Mn(CO)_3(dppe)(\mu\text{-}C\equiv C\mathit{t}Bu)]_2\}PF_6$,[3] which showed an average Cu–C distance of 2.081(1) Å and a dihedral angle of 71(1)°. The average $C\equiv C$ bond lengths in **4** (1.25(2) Å) and **7** (1.21(1) Å) are comparable to that in the manganese acetylide complex (1.237(12) Å). In the recently reported alkynyl ruthenium silver triflate complex $\{[Ru(dippe)_2]_2(\mu\text{-}Cl)_3(\sigma,\pi\text{-}C\equiv CPh)_2[Ag_2(\mu\text{-}dippe)]\}BPh_4$[25] both silver ions are coordinated to only one alkynyl moiety each; the average Ag–C bond length is 2.39(1) Å and the average $C\equiv C$ bond length is 1.25(2) Å. The average Re–C bond length is 2.15(1) Å in **4** and 2.17(1) Å in **7**, thus in **4** the longer $C\equiv C$ bond corresponds to a shorter Re–C bond than in **7**. The bend-back angles (C-C-R) at the coordinated triple bond are on average 8.9(9)° in **4** and 16.5(9)° in **7**. The corresponding angles are 9.5(10)° (C-C-Mn) in the above-mentioned manganese complex and 5.5(7)° (C-C-Ru) in the ruthenium complex. Due to the relatively large standard deviations in all these structures these bond parameters should be discussed with the necessary caution. However, the structure of the silver complex **7** appears more unusual than the copper complex **4**. It seems strange that on one hand the $C\equiv C$ bond length in **7** is shorter than in **1** or in **4**, which indicates only a very weak interaction between the Ag^+ ion and the alkyne ligand, but that on the other hand the bend-back angle is nearly twice that in **4**, and also much larger than in the two cited reference compounds, which is usually taken as an indication of a stronger interaction.[19]

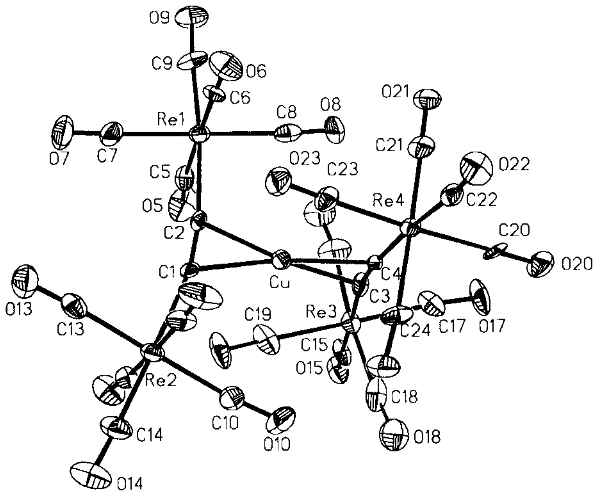


Figure 1. Structure of $[(\eta^2\text{-}\mathbf{1})_2Cu]$ (**4**) in the crystal (20% probability ellipsoids). Selected bond lengths [Å] and angles: Re1–C2 2.19(2), Re2–C1 2.15(2), C1–C2 1.22(3), C1–Cu 2.06(2), C2–Cu 2.02(2), C3–C4 1.28(3), C3–Cu 2.07(2), C3–Re3 2.11(2), C4–Cu 2.07(2), C4–Re4 2.14(2); C2-C1-Re2 167(2), C1-C2-Re1 172(2), C4-C3-Re3 171(2), C3-C4-Re4 174.3(14).

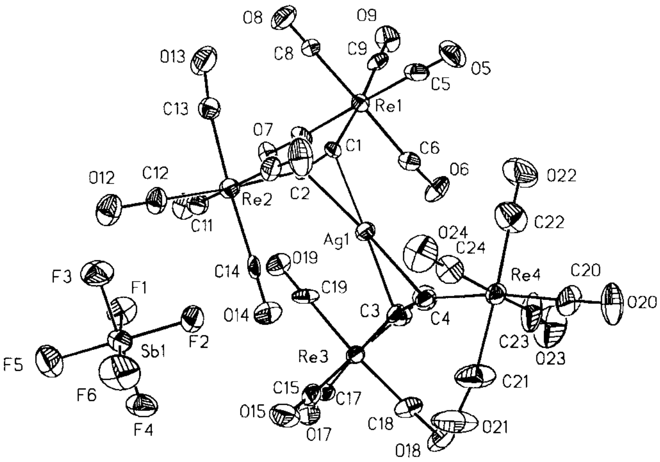


Figure 2. Structure of $[(\eta^2\text{-}\mathbf{1})_2Ag]^+$ (**7**) in the crystal (20% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Re1–C1 2.15(2), Re2–C2 2.21(2), Re3–C3 2.14(2), Re4–C4 2.17(2), Ag1–C2 2.21(2), Ag1–C1 2.24(2), Ag1–C4 2.24(2), Ag1–C3 2.32(2), C1–C2 1.21(2), C3–C4 1.21(2); C2-C1-Re1 162(2), C1-C2-Re2 163(2), C4-C3-Re3 166.0(14), C3-C4-Re4 163(2).

These structures can also be compared to a series of η^2-coordinated complexes of monometallated alkynes $[(\eta^2\text{-}RCCML_n)Cu^ICl]_n$, the copper phenanthroline complexes $[Cu(phen)(\eta^2\text{-}RCCH)]^+$, and the polymeric cyclododecadiyne complexes $[M(C_{12}H_{16})(OSO_2CF_3)]_x$ (M = Cu, Ag) (Table 2). As can be seen from these data, there is quite a strong influence of both the substituents at the acetylenic triple bond and the co-ligands at the Cu/Ag center on these bond parameters, bringing the observed values in the structures of **4** and **7** in the range of earlier structure determinations. However, the relation between the Cu and Ag complexes of **1** is different from the findings with the (polymeric) Cu and Ag complexes of cyclododecadiyne,

Table 2. Comparision of bonding parameters for compounds **4** and **7** with literature data.

Compound	Average distance between M and the C≡C [Å]	Average C≡C bond length [Å]	α [°][a]	Ref.
4	2.055 (10)	1.25(2)	8.9(9)	this work
7	2.25(1)	1.21(1)	16.5(9)	this work
$\{[L_nFeC{\equiv}CPh]CuCl\}_2$	1.99(2),	1.27(2)	18(2)	[2a]
$\{[L_nRuC{\equiv}CPh]CuCl\}$	2.025(7)	1.25(1)	7.4(8)	[2c]
$\{[L_nMnC{\equiv}CPh]CuCl\}$	2.034(3)	1.226(5)	8.9(3)	[3]
$[Cu(phen)(RC{\equiv}CH)]^+$	1.92–2.00	1.19–1.23	15–25	[19]
$[Cu(C_{12}H_{16})(OSO_2CF_3)]_x$	2.11	1.190(14)	15.6(7)	[26]
$[Ag(C_{12}H_{16})(OSO_2CF_3)]_x$	2.41	1.210(13)	10.9(6)	[26]

[a] α = bend back angle = deviation of angle C≡CR from linearity.

where the copper compound has the shorter C≡C bond length and the larger bend-back angle.

5 (Figure 3): In the crystal of **5** the PF_6 anions are strongly disordered. The structure contains a dimetallatetrahedrane Cu_2C_2. The planes Cu1-C6-C7 and Cu2-C6-C7 form an angle of 89.8°. The Cu–Cu distance is 2.786(5), the C≡C distance 1.22(3) Å, and the four Cu–C distances average to 2.06(1) Å. The sum of bond angles within the CuN_2C_2 moiety is 359.7° at Cu1 and 362.7° at Cu2, thus manifesting a planar coordination geometry around both copper centers (ignoring the second copper ion). An arrangement like this was postulated by Reger et al for $\{[Cu(bpy)]_2(alkyne)\}^{2+}$ complexes, but wasn't supported by an X-ray structure determination.[21b] The closest crystallographically characterized relatives to **5** are the tropocoronand complexes [Cu_2(TC-6,6)(ROOC-C≡C-COOR)] prepared by Lippard et al., in which the copper centers are coordinated to both alkyne carbon atoms and to two nitrogen atoms of the macrocycle, which also bridges the two copper centers.[23] The Cu–Cu distances in these complexes are 2.806(1) Å and 2.788(1) Å for R = Et and Me, respectively, and the bond angles around the copper centers sum up to 360°, parameters which are more or less identical to the values found in **5**. However, the average Cu–C distance in these complexes is about 1.95 Å and the C≡C bond lengths are 1.320(6) Å and 1.314(9), respectively; thus, much stronger Cu–C and weaker C–C bonds than in **5.** The very different N-Cu-N angles of 92.4(10)° at Cu1 and 103.9(10)° at Cu2 is quite surprising, and the reasons for this finding remain to be clarified. The bend-back angles at both carbon atoms of the triple bond average to 21(1)° in comparison to over 41° in the tropocoronand complex, which shows again a much stronger interaction between the alkyne group and the Cu ion than in **5.** However, despite of the nearly unchanged C–C bond lengths, these bond angles indicate a stronger interaction than in the 1:1 complex **4** (see above) as expected. The average Re–C bond length in **5** is 2.205(20) Å, and thus longer than in **4**, which is making up for the shorter C≡C bond (although, due to the relatively large standard deviations, the significance of these differences should not be overestimated!).

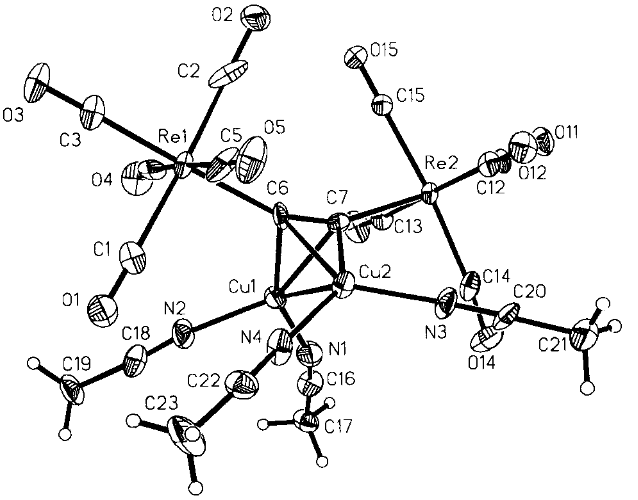


Figure 3. Structure of $[(\eta^4\text{-}\mathbf{1})Cu_2(NCMe)_4]^{2+}$ (**5**) in the crystal (20% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Re1–C6 2.19(3), Re2–C7 2.22(3), Cu1–N2 1.95(3), Cu1–N1 1.97(3), Cu1–C7 2.06(2), Cu1–C6 2.06(3), Cu1–Cu2 2.786(5), Cu2–N3 1.95(3), Cu2–N4 1.98(2), Cu2–C7 2.04(2), Cu2–C6 2.07(2), C6–C7 1.22(3); N2-Cu1-N1 92.4(10), N1-Cu1-C7 120.2(10), N2-Cu1-C6 112.7(10), C7-Cu1-C6 34.4(9), N3-Cu2-N4 103.9(10), N3-Cu2-C7 113.1(10), N4-Cu2-C6 111.2(9), C7-Cu2-C6 34.5(9), C7-C6-Re1 160(2), C6-C7-Re2 158(2).

13, 14 (Figures 4 and 5): In the dimeric complexes **13** and **14** two Cu_2C_2 tetrahedrons are bridged by four difluorophosphate anions. Both molecular structures contain a crystallographic inversion center. In **13** the average Cu–C distance is 2.043(5) Å, the average Re–C distance 2.168(7) Å, and the C≡C bond 1.275(14) Å long, while the average bend-back angle is 20.8(6)°. Thus, upon hydrolysis of **5**, the metal–carbon distances become slightly shorter, while the acetylenic triple bond elongates by 0.05 Å and the bend-back angles don't change at all. The coordination geometry around both copper centers is strictly planar (when the second Cu atom is

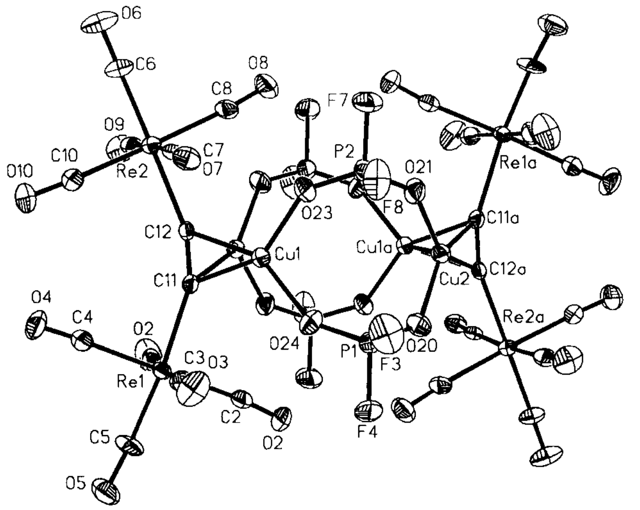


Figure 4. Structure of $[(\mathbf{1})_2Cu_4(\mu\text{-}O_2PF_2)_4]$ (**13**) in the crystal (20% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Cu2-O21 1.999(8), Cu2–O20 2.009(8), Cu2–C11A 2.011(10), Cu2–C12A 2.040(10), Cu2–Cu1A 2.622(2), O24–Cu1 1.988(8), O23–Cu1 1.995(8), Cu1–C11 2.058(10), Cu1–C12 2.063(9), C11–C12 1.275(14), C11–Re1 2.175(11), C12–Re2 2.160(10); O21-Cu2-O20 101.8(4), O21-Cu2-C11A 110.3(4), O20-Cu2-C12A 111.2(4), C11A-Cu2-C12A 36.7(4), O24-Cu1-O23 99.5(4), O24-Cu1-C11 113.1(4), O23-Cu1-C12 111.1(4), C11-Cu1-C12 36.0(4), C12-C11-Re1 157.1(8), C11-C12-Re2 161.4(8).

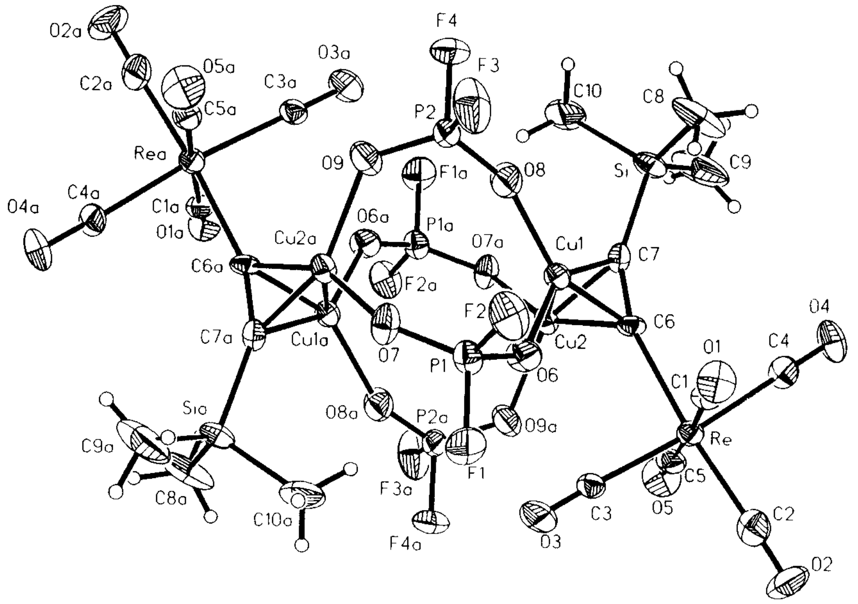


Figure 5. Structure of $[(\mathbf{2})_2Cu_4(\mu\text{-}O_2PF_2)_4]$ (**14**) in the crystal (20% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Re–C6 2.19(2), Re–C4 2.06(3), Cu1–O8 1.98(2), Cu1–O6 1.99(2), Cu1–C7 2.01(2), Cu1–C6 2.03(2), Cu1–Cu2 2.726(4), Cu2–O7A 1.99(2), Cu2–C7 1.99(2), Cu2–O9A 2.01(2), Cu2–C6 2.04(2), C6–C7 1.29(3); O8-Cu1-O6 100.7(8), O8-Cu1-C7 112.1(10), O6-Cu1-C6 109.8(8) C7-Cu1-C6 37.2(9), O7A-Cu2-C7 116.9(9), O7A-Cu2-O9A 97.2(9), C7-Cu2-C6 37.3(9), O9A-Cu2-C6 108.7(9), O7A-Cu2-Cu1 123.3(5), C7-C6-Re 161(2), C6-C7-Si 152(2).

ignored) with bond angle sums of 359.7° at Cu1 and 360.0° at Cu2, which is the same as in **5**, although the Cu–Cu distance has shortened by 0.16 Å. In **14** the dissymetry of the alkyne ligand has some minor effects on the geometrical parameters within the dimetallatetrahedrane units. The Cu–C distances to the rhenated carbon are slightly longer than those to the silylated carbon, that is 2.035(14) vs. 2.000(14) Å, the Re–C bond is 2.19(2) Å, and the acetylenic C–C triple bond is 1.29(3) Å. These bond lengths again indicate a stronger interaction of the Cu centers with the acetylenic triple bonds compared to that in **5,** although the bend-back angle in **14** of 19(2)° is even slightly smaller than in the bis(acetonitrile) complex. The coordination geometries around the copper centers are again planar with bond angle sums of 359.8° and 360.1°, but the Cu–Cu distance of 2.726(4) is closer to the value found in **5** than in **13**.

The four Cu atoms are in a plane with two short distances (**13**: 2.622 Å; **14**: 2.726 Å) and two long distances (**13**: 4.287 Å; **14**: 4.154 Å), the two Re_2C_2 ligands are perpendicular to this plane. Due to the long PO_2F_2 bridge the structures of **13** and **14** are significantly different from that of carboxylate-bridged alkynecopper(I) complexes $[(RC{\equiv}CR)_2Cu_4(\mu\text{-}RCO_2)_4]$,[20, 21c, 30] in which the four Cu atoms form (strongly) distorted tetrahedra (Table 3). Although in $[(Me_3SiC{\equiv}CSiMe_3)_2Cu_4(\mu\text{-}O_2CMe)_4]$[31] a planar arrangement of the four Cu atoms is found, the Cu–Cu distances are equal in contrast to **13** and **14**.

Conclusion

In summary, dirhenioethyne behaves as a ligand to copper(I), silver(I), and gold(I) compounds like an organic alkyne or a monometallated alkyne, and the formation of complexes with $(OC)_5ReC{\equiv}CRe(CO)_5$ as a π ligand can be considered as an experimental proof for the results of theoretical calculations on $L_nMC{\equiv}CML_n$ complexes,[9b,10d] in which only the acetylenic structure was found. $Re(CO)_5$ is isolobal[11] with the hydrogen atom or with an alkyl group, and the results presented here are further examples for this concept.[33] The stability of compounds **4**–**16** toward decomposition increases with the metal in the order Ag < Au ≪ Cu and with the ligands **2** < **1**. The light-induced reduction of silver(I) and the high tendency of gold(I) to form symmetrical complexes in contrast to copper(I) could be a reason for this behavior.

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Table 3. Comparision of X-ray data for compounds **5**, **13** and **14** with similar known structures.

	Average Cu···Cu distance [Å]	Average distance between Cu and the C≡bond [Å]	Average C≡C distance [Å]	Average angle α [°]	Ref.
$\{(\eta^2\text{-}EtC{\equiv}CEt)\ [Cu(\mu\text{-}O_2CCF_3)]_2\}_2$	2.810(2) [2 ×], 3.128(2) [4 ×]	1.976(7)	1.260(14)	27(1)	[21c]
$\{(\eta^2\text{-}EtO_2CC{\equiv}CCO_2Et)\ [Cu(\mu\text{-}O_2CC_6H_4Cl)]_2\}_2$	2.950(2) [2 ×]; 2.995(1) [3 ×], 3.129(3)[1 ×]	1.957(1)	1.287(3)	31.6(2)	[20]
$\{(\eta^2\text{-}tmtch)[Cu(\mu\text{-}O_2CCH_3)]_2\}_2$[a]	2.769(2) [2 ×], 3.136(2) [4 ×]	1.974(5)	1.259(7)	37.3(5)	[30]
$\{(\eta^2\text{-}Me_3SiC{\equiv}CCSiMe_3)\ [Cu(\mu\text{-}O_2CMe)]_2\}_2$	3.020(14)	1.992(2)	1.278(6)	21.2(2)	[31]
13	2.622(2), 4.287(2)	2.043(5)	1.275(14)	20.8(6)	this work
14	2.726(4), 4.154(4)	2.018(10)	1.29(3)	28(2)(Si–C) 19(2)(Re–C)	this work
$Cu_2(TC\text{-}6,6)\ [MeO_2CC{\equiv}CCO_2Me]$	2.788(1)	1.942(7)	1.314(4)	41.6(4)	[23]
5	2.786(5)	2.063(11)	1.22(3)	21(1)	this work

[a] tmtch = 3,3,6,6-tetramethyl-1-thia-4cyclododecadiyne.

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[33] After these studies[8b] had been completed we became aware that also the dimetalloalkyne [Cp(OC)$_2$RuC≡CRu(CO)$_2$Cp] acts as a ligand towards Cu^I and Ag^I: C. S. Griffith, G. A. Koutsantonis, A. H. White, B. W. Skelton, Abstracts Part II, XVIIIth ICOMC, Munich, August 1998, A 100.

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