Strong coordination of cycloheptynes by gold(I) chloride: synthesis and structure of two complexes of the type [(alkyne)AuCl]

Petra Schulte and Ulrich Behrens*†

Institut für Anorganische und Angewandte Chemie der Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany

Gold(I) chloride (stabilized by tetrahydrothiophene) reacts with the cycloheptynes 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne-1,1-dioxide (SO_2-alkyne) and 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne (S-alkyne) to afford the complexes $[(\eta^2\text{-alkyne})AuCl]_n$ [n = 2 (SO_2-alkyne), $n = \infty$ (S-alkyne)]; the X-ray structures of both compounds show trigonal-planar gold(I) centres and very short Au–C(alkyne) bonds.

Although gold(I) complexes (*e.g.* R_3PAuNO_3) are excellent catalysts for the addition reaction of nucleophiles to alkynes,[1] little is known about the interaction of gold(I) with the C≡C triple bond. Some efforts to prepare simple gold(I) alkyne complexes were made in 1972 by Hüttel and Wittig, but most of the obtained gold compounds were thermally unstable and all were poorly characterized.[2] In 1996–97 Lang *et al.* synthesized five stable organogold(I) 3-titanapenta-1,4-diyne complexes $[Cp_2Ti(C{\equiv}CR)_2AuR]$ with a trigonal-planar coordination of the gold(I) centre. These complexes were properly characterized, three of them by X-ray structure analysis.[3] The compounds can be considered as alkyne complexes although in reality heterometallic acetylide coordination compounds are present. Furthermore, in 1995 Mingos *et al.* reported on the compound $[Au(C{\equiv}CBu^t)]$ within the structure of which η^2(C≡C)-coordinated acetylide moieties also exist.[4]

In this study, we report on the first examples of structurally well characterized $[(\eta^2\text{-alkyne})AuCl]_n$ complexes (n = 2, ∞) with the gold(I) ion in a trigonal-planar environment. Complexes **1** and **2** were prepared by the reaction of [AuCl(tht)] (tht = tetrahydrothiophene) with equal amounts of the cycloheptynes 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne-1,1-dioxide (SO_2-alkyne) and 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne (S-alkyne), respectively (yield 90–97%).‡ Both complexes **1** and **2** form colourless crystalline powders which are thermally stable up to 150 °C. The solid compounds can be handled in air for short periods. In solution they decompose slowly when exposed to air or light. Compound **1** is soluble in tetrahydrofuran and dichloromethane, while complex **2**, due to its polymeric character in the solid state, only dissolves in strongly coordinating solvents such as mixtures of dimethyl sulfide–dichloromethane or dimethyl sulfide–tetrahydrofuran. In acetonitrile a molecular mass of 447 was found osmometrically for **1** which shows that the chloro bridges in solid **1** have been cleaved by the coordinating solvent (calc. M = 432.7 for the monomer). In chloroform a somewhat higher value (M = 580) was observed (monomer–dimer mixture in solution).

X-Ray diffraction studies were carried out on both **1** and **2** (Fig. 1 and 2).§ Compound **1** forms dimeric molecules with the gold(I) ions bridged by two chloro ligands (Fig. 1), whereas complex **2** contains a polymeric chain built up by AuCl units which are connected by S-alkyne ligands (coordination *via* the C≡C bond and the S atom; Fig. 2). The gold(I) centres exist in a trigonal-planar environment. The alkyne carbon atoms as well as the η^1-bonded Cl and S atoms are arranged in-plane, which is a typical feature for copper(I) and silver(I) η^2-alkyne complexes.[5] A very strong alkyne–gold bond is found, with the Au–C bond distances ranging from 2.050(7) to 2.100(8) Å.[6] This is close to the range for a normal Au–C-σ bond [*e.g.* Au–R-σ bond lengths of 2.00(1), 2.018(6) and 2.079(7) Å were observed for three trigonally coordinated Au^I complexes $Cp_2Ti(C{\equiv}CR)_2AuR$].[3] The C≡C bonds are lengthened from 1.194 Å (C≡C bond distance for the free SO_2-alkyne)[7] and 1.209 Å (C≡C bond distance for the free S-alkyne)[7] to 1.259(11) Å (**1**) and 1.244(11) Å (**2**), which also proves the existence of a strong Au–η^2(C≡C) interaction. For a gold(I) complex with trigonal-planar coordination, an extremely short Au–Cl bond length of 2.409(2) Å is observed in **2**. For instance, in the complex $(Ph_3P)_2AuCl$, an Au–Cl distance above 2.50 Å is observed.[8] A value of about 2.40 Å, as in **2**, is normally found for Au–Cl bonds in square-planar neutral organyl Au^{II} complexes.[9] We therefore think that strong back-bonding from Au^I to the cycloalkyne ligand occurs in **2** (and also in **1**), which is equivalent to partial oxidation of the Au^I ion to Au^{III}. Also complex **1** is the first example of a gold(I) complex where two chloro ligands bridge two Au^I ions.[10] In gold(III) chemistry such bridging chloro ligands are only known for the structure of gold(III) chloride.[11] No aurophilic attractions (weak inter- or intramolecular $Au^I \cdots Au^I$ interactions resulting in Au–Au distances shorter than 3.40 Å) between the Au^I ions are found in **1** or **2**.[12] The intramolecular

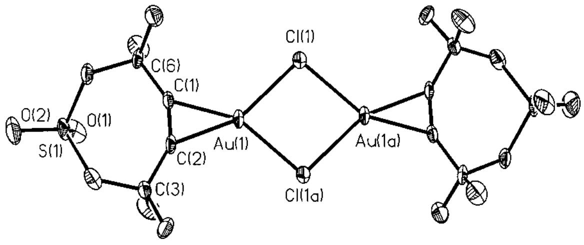

Fig. 1 View of the molecular structure of $[AuCl(SO_2\text{-alkyne})]_2$ **1** with atomic numbering scheme (60% thermal ellipsoids). Selected bond lengths (Å) and angles (°): Au(1)···Au(1a) 3.666(1), Au(1)–Cl(1) 2.456(2), Au(1)–Cl(1a) 2.473(3), Au(1)–C(1) 2.075(9), Au(1)–C(2) 2.055(9), C(1)–C(2) 1.259(12); Cl(1)–Au(1)–Cl(1a) 83.9(1), Cl(1)–Au(1)–C(1) 121.4(2) Cl(1a)–Au(1)–C(2) 119.2(3), C(1)–Au(1)–C(2) 35.5(3), Au(1)–Cl(1)–Au(1a) 96.1(1), C(2)–C(1)–C(6) 147.3(8), C(1)–C(2)–C(3) 146.4(9).

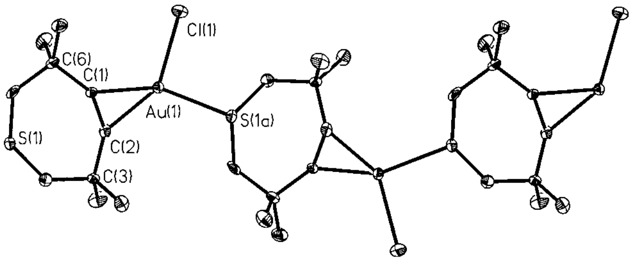

Fig. 2 Part of the polymeric chain of solid [AuCl(S-alkyne)] **2** with atomic numbering scheme (60% thermal ellipsoids). Selected bond lengths (Å) and angles (°): Au(1)–Cl(1) 2.409(2), Au(1)–S(1a) 2.415(2), Au(1)–C(1) 2.050(7), Au(1)–C(2) 2.100(8), C(1)–C(2) 1.244(11); Cl(1)–Au(1)–S(1a) 96.1(1), Cl(1)–Au(1)–C(1) 110.5(2), S(1a)–Au(1)–C(2) 118.7(2), C(1)–Au(1)–C(2) 34.9(3), C(2)–C(1)–C(6) 146.3(7), C(1)–C(2)–C(3) 146.6(7).

Au···Au distance in **1** is 3.666(1) Å; the Au–Cl–Au angle is 96.1(1)°.

The strong η^2-coordination of the alkyne triple bond is also confirmed by IR spectroscopy. The C≡C stretching vibration is shifted from 2177 cm^{-1} to 1949, 1928 cm^{-1} (**1**) and from 2188, 2161 cm^{-1} to 1930, 1910 cm^{-1} (**2**). These shifts of about 250 cm^{-1} are much larger than those found in cycloheptyne copper(I) chloride complexes (180 cm^{-1}).[13]

This study shows that angle-strained alkynes are able to interact strongly with the gold(I) ion, thus forming thermally stable complexes. An investigation of the coordination behaviour of other alkynes with gold(I) is in progress.

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Notes and References

† behrens@xray.chemie.uni-hamburg.de

‡ *Experimental data* for **1**: [AuCl(tht)][14] (1.00 g, 3.1 mmol) was suspended at 0 °C in tetrahydrofuran (30 ml). 3,3,6,6-Tetramethyl-1-thiacyclohept-4-yne-1,1-dioxide[15] (0.75 g, 3.7 mmol) was added and the solution stirred at 0 °C for 1 h. The clear solution was evaporated to dryness to remove the released tetrahydrothiophene. Cyclopentane (25 ml, 0 °C) was added to extract excess alkyne ligand. Filtration of the precipitate (washed twice with 3 ml cyclopentane) gave a yield of 1.2 g (2.8 mmol, 90%) of complex **1** in the form of a colourless crystalline powder (mp 176 °C, decomp.). The compound is insoluble in cyclopentane and benzene, but soluble in acetonitrile, dichloromethane, chloroform and tetrahydrofuran. IR (KBr) ν/cm^{-1} 1949, 1928; ^1H NMR (200 MHz, $CDCl_3$) δ 1.39 (s, 12H, CH_3), 3.32 (s, 4H, CH_2); ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 27.89 (CH_3), 30.35 (CCH_3), 66.76 (CH_2), 97.15 (C≡C); elemental analysis: found C 28.07, H 3.97%; calc. C 27.76, H 3.73%. For **2**: [AuCl(tht)][14] (1.00 g, 3.1 mmol) was suspended at 0 °C in tetrahydrofuran (25 ml). 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne[16] (0.9 g, 5.3 mmol) was added and the slurry stirred at 20 °C (3 days, exclusion of light). The mixture was evaporated to dryness to remove the released tetrahydrothiophene. Tetrahydofuran (20 ml) was added to extract excess alkyne ligand. Filtration of the precipitate (washed twice with 3 ml tetrahydrofuran) gave a yield of 1.2 g (3.0 mmol, 97%) of complex **2** in the form of a colourless crystalline powder (mp 245 °C, decomp.). The compound is insoluble in acetonitrile, benzene, dichloromethane, chloroform and tetrahydrofuran, but soluble in tetrahydrothiophene, dimethyl sulfide, and in mixtures of dimethyl sulfide with dichloromethane and tetrahydrofuran. IR (KBr) ν/cm^{-1} 1930, 1910; elemental analysis: found C 30.07, H 3.99%; calc. C 29.97, H 4.03%.

§ Single crystals of **1** were grown from a solution in tetrahydrofuran to which cyclopentane was slowly added *via* the gas phase. Single-crystals of **2** were grown from a solution in dichloromethane–dimethyl sulfide (15 : 1) to which cyclopentane was slowly added *via* the gas phase.

Crystal data for **1**: $C_{10}H_{16}AuClO_2S$, $M = 432.70$, triclinic, space group $P\bar{1}$, $a = 6.897(9)$, $b = 8.563(2)$, $c = 11.957(3)$ Å, $\alpha = 75.68(1)$, $\beta = 78.41(4)$, $\gamma = 69.54(4)$°, $U = 635.9(9)$ Å^3, $Z = 2$, $D_c = 2.260$ g cm^{-3}, μ(Mo-Kα) = 11.92 mm^{-1} (absorption correction by the ψ scan method). P4 Siemens diffractometer, using θ–2θ scan technique [2θ limits 5.0–55.0°] and Mo-Kα radiation ($\lambda = 0.71073$ Å). Crystal dimensions: 0.6 × 0.6 × 0.25 mm, 2397 observed data [$I \geqslant 2\sigma(I)$] of 2575 independent data measured ($T = 173$ K). Refinement (on F^2) to $R_1 = 0.048$ and $wR_2 = 0.127$. No. of refined parameters: 143. For **2**: $C_{10}H_{16}AuClS$, $M = 400.72$, monoclinic, space group $P2_1/n$, $a = 8.880(2)$, $b = 13.547(2)$, $c = 10.513(2)$ Å, $\beta = 109.93(2)$°, $U = 1188.9(4)$ Å^3, $Z = 4$, $D_c = 2.239$ g cm^{-3}, μ(Mo-Kα) = 12.73 mm^{-1} (absorption correction carried out with DIFABS program).[17] P4 Siemens diffractometer, using θ–2θ scan technique [2θ limits 5.0–55.0°] and Mo-Kα radiation ($\lambda = 0.71073$ Å). Crystal dimensions: 0.6 × 0.4 × 0.1 mm, 2307 observed data [$I \geqslant 2\sigma(I)$] of 2735 independent data measured ($T = 173$ K). Refinement (on F^2) to $R_1 = 0.046$ and $wR_2 = 0.116$. No. of refined parameters: 125. In both structures all atoms (excluding hydrogens) were refined using anisotropic displacement parameters (riding model for hydrogens). The structures were solved by direct methods (SHELXS-86 and SHELXL-93).[18] CCDC 182/915.

1 J. H. Teles, S. Brode and M. Chabanas, *Angew. Chem.*, 1998, **110**, 1475; *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 1415. For the catalytic effect of the $[AuCl_4]^-$ anion, see Y. Fukuda and K. Utimoto, *J. Org. Chem.*, 1991, **56**, 3729; *Bull. Chem. Soc. Jpn.*, 1991, **64**, 2013.

2 R. Hüttel and H. Forkl, *Chem. Ber.*, 1972, **105**, 1664; G. Wittig and S. Fischer, *Chem. Ber.*, 1972, **105**, 3542. For the general literature on alkyne complexes of gold and on alkynylgold(I) compounds, see H. Schmidbaur, in *Organogold Compounds, Gmelin Handbook of Inorganic Chemistry*, Springer Verlag, Berlin, 1980, pp. 209–211 and 191–194; A. Grohmann and H. Schmidbaur, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Elsevier Science, Oxford, 1995, vol. 3, pp. 44 and 6–9; R. J. Puddephatt, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 2, pp. 812–814 and 766–774.

3 H. Lang, K. Köhler and L. Zsolnai, *Chem. Commun.*, 1996, 2043; K. Köhler, S. J. Silverio, I. Hyla-Kryspin, R. Gleiter, L. Zsolnai, A. Driess, G. Huttner and H. Lang, *Organometallics*, 1997, **16**, 4970.

4 D. M. P. Mingos, J. Yau, S. Menzer and D. J. Williams, *Angew. Chem.*, 1995, **107**, 2045; *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1894.

5 H. Lang, K. Köhler and S. Blau, *Coord. Chem. Rev.*, 1995, **143**, 113; P. Schulte and U. Behrens, *J. Organomet. Chem.*, 1998, in press, and references therein.

6 Considerably longer Au–η^2(C≡C) bond lengths were found for the complexes $Cp_2Ti(C{\equiv}CR)_2AuR$ [2.22(1)–2.27(1) Å].[3]

7 P. J. Stang and F. Diederich, *Modern Acetylene Chemistry*, VCH Verlagsgesellschaft, Weinheim, 1995, p. 296.

8 N. C. Baenziger, K. M. Dittemore and J. R. Doyle, *Inorg. Chem.*, 1974, **13**, 805; G. A. Bowmaker, J. C. Dyson, P. C. Healy, L. M. Engelhardt, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1987, 1089.

9 H. Schmidbaur, J. R. Mandl, A. Frank and G. Huttner, *Chem. Ber.*, 1976, **109**, 466; H. H. Murray III, J. P. Fackler, Jr., L. C. Porter and A. M. Mazany, *J. Chem. Soc., Chem. Commun.*, 1986, 321.

10 In copper(I) chloride alkyne complexes this type of structure is quite common: H. Lang, K. Köhler and S. Blau, *Coord. Chem. Rev.*, 1995, **143**, 113; P. Schulte, G. Schmidt, C.-P. Kramer, A. Krebs and U. Behrens, *J. Organomet. Chem.*, 1997, **530**, 95, and references therein. On the other hand, gold(I) chloride alkene complexes show linear coordination geometry at the metal: D. B. Dell'Amico, F. Calderazzo, R. Dantona, J. Strähle and H. Weiss, *Organometallics*, 1987, **6**, 1207.

11 E. S. Clark, D. H. Templeton and C. H. MacGillavry, *Acta Crystallogr.*, 1958, **11**, 284.

12 H. Schmidbaur, *Chem. Soc. Rev.*, 1995, 391; P. Pyykkö, N. Runeberg and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1451; P. Pyykkö and F. Mendizabal, *Chem. Eur. J.*, 1997, **3**, 1458.

13 P. Schulte, G. Schmidt, C.-P. Kramer, A. Krebs and U. Behrens, *J. Organomet. Chem.*, 1997, **530**, 95.

14 R. Usón and A. Laguna, *Organomet. Synth.*, 1986, **3**, 322.

15 U. Höpfner, diploma, University of Heidelberg, 1976.

16 A. Krebs and H. Kimling, *Tetrahedron Lett.*, 1970, 761; *Liebigs Ann. Chem.*, 1974, 2074.

17 A. L. Spek, DIFABS, Part of program PLATON95, *Acta Crystallogr., Sect. A*, 1990, **46**, C34; N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

18 G. M. Sheldrick, Program for Crystal Structure Solution (SHELXS) and Program for Crystal Structure Refinement (SHELXL), University of Göttingen, 1986 and 1993.

Received in Cambridge, UK, 20th May 1998; 8/03791D