# Unusual coordination mode of organogold(I) compounds: trigonal-planar complexation of gold(I) centres by alkynes

**Heinrich Lang,*† Katrin Köhler and Laszlo Zsolnai**

*Ruprecht-Karls-Universität Heidelberg, Anorganisch-Chemisches Institut, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany*

**Linearly directed donor-stabilized organogold(I) compounds react with the 3-titanopenta-1,4-diyne [($\eta^5$-$C_5H_4SiMe_3$)$_2$Ti(C≡CSiMe$_3$)$_2$]T 1 to afford complexes 1·Au($\eta^1$-R) [R = Me 3a, $C_6H_2(CF_3)_3$-2,4,6 3b, C≡CSiMe$_3$ 3c] in which the gold(I) centre possesses a trigonal-planar environment formed by two $\eta^2$-coordinated alkyne units and a $\eta^1$-bonded organic group R; the X-ray structure analysis of [{($\eta^5$-$C_5H_4SiMe_3$)$_2$Ti(C≡CSiMe$_3$)$_2$}-Au{$\eta^1$-$C_6H_2(CF_3)_2$-2,4,6}] 3b is reported.**

Organogold(I) compounds, Au–R, generally exist as polynuclear species.[1–4] These molecules can be broken down to monomeric L→AuR compounds (R = singly bonded organic ligand; L = Lewis-base containing N, P or S donors) in which the gold atoms maintain the coordination number two, with a linear L–Au–R arrangement.[4b,5,6] The same arrangement is obtained when dipodal ligands, such as dppe, are applied, leading to molecules with two AuR moieties. This behaviour appears to be caused by Au···Au interactions between the seemingly closed-shell group 11 metal centres.[4,7,8]

In this study, we report of first examples of monomeric bis($\eta^2$-alkyne)Au($\eta^1$-R) complexes, [{($\eta^5$-$C_5H_4SiMe_3$)$_2$Ti-(C≡CSiMe$_3$)$_2$}Au($\eta^1$-R)] (R = singly bonded organic ligand), with a gold atom in a trigonal-planar environment, which result from the reactions of LAuR with the well designed organometallic chelate [($\eta^5$-$C_5H_4SiMe_3$)$_2$Ti(C≡CSiMe$_3$)$_2$] **1**.

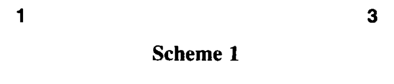
The bis(alkynyl) titanocene **1** reacted at −70 to 0 °C in diethyl ether with 1 mol equiv. of *in-situ* prepared [AuR(SMe$_2$)] [R = Me **2a**, $C_6H_2(CF_3)_2$-2,4,6 **2b**, C≡CSiMe$_3$ **2c**][9] to form pale orange [{($\eta^5$-$C_5H_4SiMe_3$)$_2$Ti(C≡CSiMe$_3$)$_2$}Au($\eta^1$-R)] [R = Me **3a**, $C_6H_2(CF_3)_3$-2,4,6 **3b**, C≡CSiMe$_3$ **3c**] in 60–75% yield (Scheme 1).‡

After appropriate purification, orange crystals of products **3a–c** could be obtained, which are stable for months in the solid state. Remarkably, solid compounds **3a–c** can be handled in air for short periods, while they slowly start to decompose in solution on being exposed to air.

Compounds **3a–c** are monomeric in solution (cryoscopy in benzene) and their EI mass spectra are in agreement with this monomeric character.

In order to establish the solid-state structure of molecules **3a–c** an X-ray diffraction study was examplarily carried out on single crystals of **3b** (Fig. 1).§

The molecular structure of the heterobimetallic complex **3b** in the solid state shows that it contains a gold atom, which is trigonally coordinated by an $\eta^1$-bonded $C_6H_2(CF_3)_3$-2,4,6 group and a chelating bis(alkynyl) titanocene fragment (Fig. 1). Complex **3b** is the first example of a monomeric aryl gold(I) entity stabilized by alkyne ligands. The gold(I) centre possesses a trigonal-planar environment,[10] comprising two $\eta^2$-coordinated C≡C building blocks [C(17)–C(18), C(19)–C(20)] and the $\eta^1$-bonded ligand $C_6H_2(CF_3)_3$-2,4,6 [C(25)]. The alkyne carbon atoms [C(17), C(18), C(19), C(20)], the silicon atoms Si(3) and Si(4), the metal atoms Au and Ti as well as the aryl $C_{ipso}$ atom C(25) are arranged in-plane (maximum atomic deviation 0.088 Å). This is consistent with $\eta^2$-alkyne-to-group 11 metal bonding, typically found in $\eta^2$-alkyne stabilized monomeric copper(I) and silver(I) compounds of general type [{($\eta^5$-$C_5H_4SiMe_3$)$_2$Ti(C≡CSiMe$_3$)$_2$}MR] (M = Cu, Ag).[11–13] Accordingly, the following characteristic features of this bonding situation are: (*i*) the lengthening of the C≡C bonds from 1.203(9) and 1.214(6) Å (the uncoordinated C≡C bond distances in the organometallic chelate **1**)[14] to 1.220(10) Å [C(17)–C(18)] and 1.250(10) Å [C(19)–C(20)] in **3b**, and (*ii*) bending of the Ti–C≡C–Si units from linearity in molecule **1** [Ti–C≡C 175.8(4)/178.2(5)°, C≡C–Si 174.8(4)/178.3(5)°] to 162.1(6)° [Ti–C(17)–C(18)] or 162.4(7)° [Ti–C(19)–C(20)] and 155.3(7)° [C(17)–C(18)–Si(3)] or 156.3(7)° [C(19)–C(20)–Si(4)] in **3b**, respectively (Fig. 1). The plane formed by the atoms Au and C(25)–C(33) is almost perpendicular to the Ti,C(17)–C(20),Si(3),Si(4),Au plane (interplanar angle 86.8°). The two-electron–two-centre (2e–2c) Au–C(25) bond length at 2.079(7) Å in compound **3b** fits perfectly into the range expected for this type of bonding.[15] Moreover, as a result of the $\eta^2$-coordination of both C≡C triple bonds to the gold(I) centre the bite angle C(17)–Ti–C(19) in the free organometallic chelate **1** decreases from 102.8(2) to 95.4(3)° in heterobimetallic **3b** (Fig. 1).[14] Likewise, the Ti–Au distance of



Scheme 1

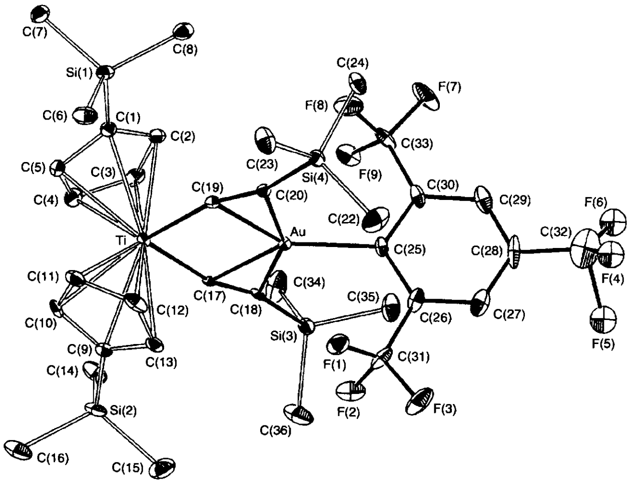


**Fig. 1** ORTEP drawing (50% probability level) **3b**. Selected bond distances (Å) and angles (°): Ti–Au 2.9948(14), Au–C(25) 2.079(7), Au–C(17) 2.217(7), Au–C(18) 2.245(7), Au–C(19) 2.217(8), Au–C(20) 2.245(8), C(17)–C(18) 1.220(10), C(19)–C(20) 1.250(10); Ti–C(17)–C(18) 162.1(6), Ti–C(19)–C(20) 162.4(7), C(17)–C(18)–Si(3) 155.3(7), C(19)–C(20)–Si(4) 156.3(7), Ti–Au–C(25) 179.4(2), C(17)–Ti–C(19) 95.4(3), D(1)–Ti–D(2) 134.6 [D(1), D(2) are centroids of the cyclopentadienyl ligands].§

2.9948(14) Å is relatively short, as compared to characteristic Ti–Cu or Ti–Ag distances in isostructural $[\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2\}MR]$ compounds.[11–13] Because of this, *ab initio* molecular orbital calculations were carried out for $[\{(\eta^5\text{-}C_5H_5)_2Ti(C\equiv CH)_2\}M(\eta^1\text{-}C\equiv CH)]$ (M = Cu, Au).[16] Calculated atomic charges and Wiberg bond indices show a larger Ti–M interaction for Ti–Au, as compared to Ti–Cu.[16] This finding is in accord with the relatively short Ti–Au bond distance found in heterobimetallic **3b**. Short metal–gold distances are also observed in other metal–gold complexes.[17]

The $\eta^2$-coordination of the C≡C entities to a monomeric $Au(\eta^1\text{-}R)$ moiety is additionally confirmed by IR spectroscopy. The C≡C stretching vibration is shifted from 2012 $cm^{-1}$ in compound **1**[14,18] to 1830 $cm^{-1}$ in **3b**, 1831 $cm^{-1}$ in **3a** or 1848 $cm^{-1}$ in **3c**, indicating a weaker carbon–carbon triple bond in the coordination complexes **3a–c**.‡

On $\eta^2$-coordination of the alkynyl ligands to the gold(I) centre in the $^{13}C\{^1H\}$ NMR spectra of compounds **3a–c** the resonance signal of the $C_\alpha$ atoms is shifted slightly downfield (δ 172.4 **1**,[14,18] 199.1 **3a**, 183.5 **3b**, 181.1 **3c**), while the $C_\beta$ carbon atoms are shifted to higher field (δ 135.4 **1**,[14,18] 122.6 **3a**, 123.5 **3b**, 122.0 **3c**). These data are in agreement with the observation generally made by changing from non-coordinated to $\eta^2$-coordinated 3-metallopenta-1,4-diynes.[11–14]

The result of this study shows that the capability of the organometallic π-tweezer **1** to stabilize mononuclear organometallic fragments now gives entry to mononuclear gold(I) species. In the heterobimetallic titanium–gold compounds obtained, both alkyne moieties of the bis(alkynyl) titanocene are $\eta^2$-coordinated to the gold atom, giving rise to a unusual trigonal-planar coordination mode in organogold(I) chemistry.

This work was supported in part by the Fonds der Chemischen Industrie, the Deutsche Forschungsgemeinschaft and the Hermann-Schlosser Stiftung, Degussa AG Frankfurt (K. K.). We are grateful to Professor Dr H. W. Roesky for a generous gift of $C_6H_3(CF_3)_3$-1,3,5.

## Footnotes

† *Present address*: Technische-Universitát Chemuitz-Zwickan, Institut für Chemie, Lehrstuhl Anorganische Chemie, Straße der Nationen 62, D-09107 Chemuitz, Germany.

‡ With respect to compounds **3a–c** representative experimental data are given for **3b**: $C_6H_3(CF_3)_3$-1,3,5 (0.11 g, 0.39 mmol) was deprotonated at 0 °C in diethyl ether (50 ml) with $Bu^nLi$ (0.17 ml, 0.39 mmol, 2.3 mol $dm^{-3}$ BuLi in hexane). After stirring for 1 h, $[AuCl(SMe_2)]$[19] (0.10 g, 0.39 mmol) was added, and under simultaneous precipitation of LiCl, $[Au\{C_6H_3(CF_3)_3\text{-}2,4,6\}(SMe_2)]$ was formed. After 30 min the reaction mixture was treated with **1**[18] (0.20 g, 0.39 mmol). After filtration through Celite the solution was concentrated to yield pale orange crystals upon cooling to 0 °C. Yield: 0.30 g (77%) of **3b**, mp 118 °C (decomp.); IR (KBr) $\nu/cm^{-1}$ 1830 (C≡C); $^1H$ NMR (200.13 MHz, $C_6D_6$) δ 0.04 (s, 18 H, $SiMe_3$), 0.27 (s, 18 H, $SiMe_3$), 5.22 (pseudo t, 4 H, $C_5H_4$, $J_{HH}$ 2.3 Hz), 5.75 (pseudo t, 4 H, $C_5H_4$, $J_{HH}$ 2.3 Hz), 8.17 (s, 2 H, $C_6H_2$); $^{13}C$ NMR (55.33 MHz, $C_6D_6$) δ 0.5 ($SiMe_3$), 0.7 ($SiMe_3$), 111.1 ($C_5H_4$), 113.0 ($C_5H_4$), 116.5 (*ipso*-C, $C_5H_4$), 123.5 (C≡*C*Si), 123.8 (*m*-$C_6H_2$), 124.4 (AuC), 139.9 (q, *ipso*-C, $C_6H_2$, $^2J_{CF}$ 28.4 Hz), 183.5 (Ti*C*≡C); $CF_3$ could not unambiguously be assigned; EIMS, *m*/*z* (rel. intens.) 994 (40) ($M^+$), 616 (55) $[M^+ - C_6H_2(CF_3)_3 - C_2SiMe_3]$, 516(45) $[M^+ - AuC_6H_2(CF_3)_3]$, 322(100) $[(C_5H_4SiMe_3)_2Ti^+]$.

Spectroscopic data for compounds **3a** and **3c**: **3a**: mp 55 °C (decomp.); IR (KBr) $\nu/cm^{-1}$ 1831 (C≡C); $^1H$ NMR (200.13 MHz, $C_6D_6$) δ 0.27 (s, 18 H, $SiMe_3$), 0.46 (s, 18 H, $SiMe_3$), 1.70 (s, 3 H, Me), 4.97 (pseudo t, 4 H, $C_5H_4$, $J_{HH}$ 2.3 Hz), 5.61 (pseudo t, 4 H, $C_5H_4$, $J_{HH}$ 2.3 Hz); $^{13}C$ NMR (55.33 MHz, $C_6D_6$) δ −10.3 (AuMe), 0.6 ($SiMe_3$), 1.1 ($SiMe_3$), 109.0 ($C_5H_4$), 112.3 ($C_5H_4$), 115.9 (*ipso*-C, $C_5H_4$), 122.6 (C≡*C*Si), 199.1 (Ti*C*≡C).

**3c**: mp 105 °C (decomp.); IR (KBr) $\nu(C\equiv C)/cm^{-1}$ 2054s ($AuC\equiv CSiMe_3$), 1848m ($\eta^2\text{-}TiC\equiv CSiMe_3$); $^1H$ NMR (200.13 MHz, $C_6D_6$) δ 0.20 (s, 18 H, $SiMe_3$), (s, 0.39 H, $SiMe_3$), 0.63 (s, 18 H, $SiMe_3$), 4.94 (pseudo t, 4 H, $C_5H_4$, $J_{HH}$ 2.3 Hz), 5.58 (pseudo t, 4 H, $C_5H_4$, $J_{HH}$ 2.3 Hz); $^{13}C$ NMR (55.33 MHz, $C_6D_6$) δ 0.6 ($SiMe_3$), 1.0 ($SiMe_3$), 1.5 ($SiMe_3$), 110.4 ($C_5H_4$), 113.2 ($C_5H_4$), 116.9 (ipso-*C*, $C_5H_4$), 122.0 (C≡*C*Si), 123.4/129.6 (Au*C*≡$CSiMe_3$), 181.1 (Ti*C*≡C); EIMS, *m*/*z* (rel. intens.) 810(20) ($M^+$), 613(40) ($M^+ - 2\,C_2SiMe_3$), 418(5) ($M^+ - AuC_2SiMe_3 - C_2SiMe_3$), 322(100) $[(C_5H_4SiMe_3)_2Ti^+]$, 73(25) ($SiMe_3^+$).

§ *Crystal data* for **3b**: $C_{35}H_{46}AuF_9Si_4Ti$, $M = 994.20$, monoclinic, space group $P2_1/c$; $a = 15.730(4)$, $b = 12.959(2)$, $c = 20.334(3)$ Å, $\beta = 88.35(1)°$; $U = 4143(1)$ $Å^3$, $Z = 4$, $D_c = 1.595$ g $cm^{-3}$. R3m/v Siemens diffractometer, using the θ–2θ technique [2θ limits: 4.0–47.0°, scan range 0.5°, scan speed: $14.0 \leqslant d\omega/dt \leqslant 14.0°$ $min^{-1}$ (in 2θ)] and Mo-Kα radiation (λ = 0.71069 Å), graphite monochromator. Crystal dimensions: 0.30 × 0.30 × 0.30 mm, 4521 observed data $[I \geqslant 2\sigma(I)]$ of 6369 data measured ($T$ = 200 K) were refined to $R_1 = 0.047$ and $R_w = 0.106$ ($F^2$ refinement). No. of refined parameters: 460. Max. residual electron density = 1.70 e $Å^{-3}$. Transmission factors for absorption correction: min., max. 66, 99%.

The atoms F(4)–F(6) at C(32) are disordered (rotation disordering 45°). Anisotropic refinement of F(4)–F(6) with restraints SAME, SIMU & DELU was not possible. All atoms were refined anisotropically, excluding the hydrogen atoms and disordered F(4)–F(6) atoms. The hydrogen atoms were placed in calculated positions, and their thermal parameters were refined isotropically. The structure was solved by direct methods (SHELXS-86[20] and SHELXL-93[21]). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/173.

## References

1 R. J. Puddephatt, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, ch. 15, p. 765.
2 H. Schmidbaur and A. Grohmann, in *Comprehensive Organometallic Chemistry II*, Elsevier Science, Oxford, 1995.
3 H. Schmidbaur, in *Organogold Compounds, Gmelin Handbook of Inorganic Chemistry*, Springer Verlag, Berlin, 1980.
4 (*a*) 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 and references therein; (*b*) D. M. P. Mingos, *J. Chem. Soc., Dalton Trans.*, 1996, 561.
5 A. Gräfe and T. Kruck, *J. Organomet. Chem.*, 1996, **506**, 31 and references therein.
6 T. E. Müller, S. W. Choi, D. M. P. Mingos, D. Murphy, D. J. Williams and V. W. Yam, *J. Organomet. Chem.*, 1994, **484**, 209.
7 N. C. Payne, R. J. Puddephatt, R. Ravindranath and I. Treurnicht, *Can. J. Chem.*, 1988, **66**, 3176.
8 E. J. Fernandez, M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna, J. M. Lopez-de-Luzuriaga and M. A. Rodriguez, *Chem. Ber.*, 1995, **128**, 121.
9 Compounds $[AuR(SMe_2)]$ **2** were synthesized according to: R. Uson, A. Laguna and J. Vicente, *J. Organomet. Chem.*, 1977, **131**, 471.
10 For a distorted trigonal organogold(I) complex see: J. Vicente, A. Arcas, P. G. Jones and J. Lautner, *J. Chem. Soc., Dalton Trans.*, 1990, 451.
11 H. Lang and M. Weinmann, *Synlett*, 1996, 1.
12 H. Lang, K. Köhler and S. Blau, *Coord. Chem. Rev.*, 1995, **143**, 113.
13 H. Lang, K. Köhler and M. Büchner, *Chem. Ber.*, 1995, **128**, 525.
14 H. Lang, M. Herres and L. Zsolnai, *Organometallics*, 1993, **12**, 5008.
15 A. Sladek, S. Hofreiter, M. Paul and H. Schmidbaur, *J. Organomet. Chem.*, 1995, **501**, 47.
16 For a detailed analysis of the bonding in $[\{(\eta^5\text{-}C_5H_5)_2Ti(C\equiv CH)_2\}M(\eta^1\text{-}C\equiv CH)]$ (M = Cu, Au) see: D. Köhler, A. Driess, L. Zsolnai, S. J. Silverio, I. Hyla-Kryspin, R. Gleiter and H. Lang, *Organometallics*, to be submitted; M. D. Janssen, K. Köhler, M. Herres, A. Dedieu, W. J. J. Smeets, A. L. Spek, D. M. Grove, H. Lang and G. van Kolten, *J. Am. Chem. Soc.*, 1996, **118**, 4817.
17 For example: H. Yip, H. Lin, Y. Wang and C. Che, *J. Chem. Soc., Dalton Trans.*, 1993, 2939.
18 H. Lang and D. Seyferth, Z. *Naturforsch., Teil B*, 1990, 212.
19 Y. Yang, V. Ramamoorthy and P. R. Sharp, *Inorg. Chem.*, 1993, **32**, 1946.
20 SHELXS-86, G. M. Sheldrick, Program for Crystal Structure Solution, University of Göttingen, 1986.
21 SHELXL-93, G. M. Sheldrick, Program for Crystal Structure Refinement, University of Göttingen, 1993.

*Received, 27th June 1996; Com. 6/04480H*