

18-Membered Heterometallacyclic Gold(I) Compounds: Structural Influences of Co-crystallized Solvent

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Dedicated to Professor Heribert Offermans on the occasion of his 75th birthday

5-Lithiated 4,4-dimethyl-2-(2-thienyl)oxazoline reacted by halide and tetrahydrothiophene (THT) substitution with [AuCl(THT)] to form a cyclic trinuclear compound (**1**) in satisfactory yield. Spectroscopic studies and single-crystal X-ray analyses clarified the bonding within the ring system. The structure determination of two THF solvates revealed differences in the supramolecular assembly of the constituting molecules.

Key words: Heterometallacyclic Complexes, Carbene Character, Gold, Thienyl Oxazoline, Crystal Modification

Introduction

We have previously shown that by using consecutive selective lithiation [1], transmetallation and alkylation, 5-thienylidene complexes of selected transition metals can readily be prepared from 4,4-dimethyl-2-(thien-2-yl) oxazoline [2, 3]. However, when we attempted similar reactions using the 3-lithiated isomer of the same bifunctional oxazoline there were some complications during the first reaction step, depending on the metal halide complex used. In a reaction with [FeCp(CO)₂Cl], one of the carbonyl ligands is intramolecularly attacked by the nucleophilic nitrogen atom of the oxazoline ring to afford a neutral, dinuclear, 6-membered heterometallacyclic chelate (**I**, Fig. 1) [2]. In a reaction with [AuCl(THT)], the remote nitrogen atom again displays its nucleophilic character in displacing the labile THT ligand from the gold complex to form a neutral, 10-membered digold heterometallacycle (**II**, Fig. 1) [4].

The potential for carbene-like electron arrangement in the ligands of both **I** and **II** is clear from the contribut-

ing structures shown in Fig. 1. Whereas [FeCp(CO)₂Cl] reacts by simple Cl[−] substitution with the 5-lithiated reactant, initial experiments have previously shown that both ligands in [AuCl(THT)] are substituted by the carbanionic carbon on one ligand and an imine N atom on another. The formation of the resulting 18-membered ring has been briefly commented on [4]. Publication of its crystal structure based on rather unsatisfactory crystal data, was, however, not justified.

In recent related research that afforded the first example of a gold rotaxane, the linear cationic gold complex [Au(PMe₃)₂]⁺ was installed in another neutral 18-membered ring system assembled by substitutive carbene and acetylide interactions with a labile gold(I) complex (**III**, Fig. 1) [5]. Furthermore, some of us have reported the interaction of cyclic metal-organic rings with gases, solvent molecules and dissolved substances [6–9].

In this paper we i) report the isolation and X-ray characterization of two large-ring gold solvates; ii) explain the effect of varying solvent accommodation on the crystal and molecular structure of the cyclic prod-

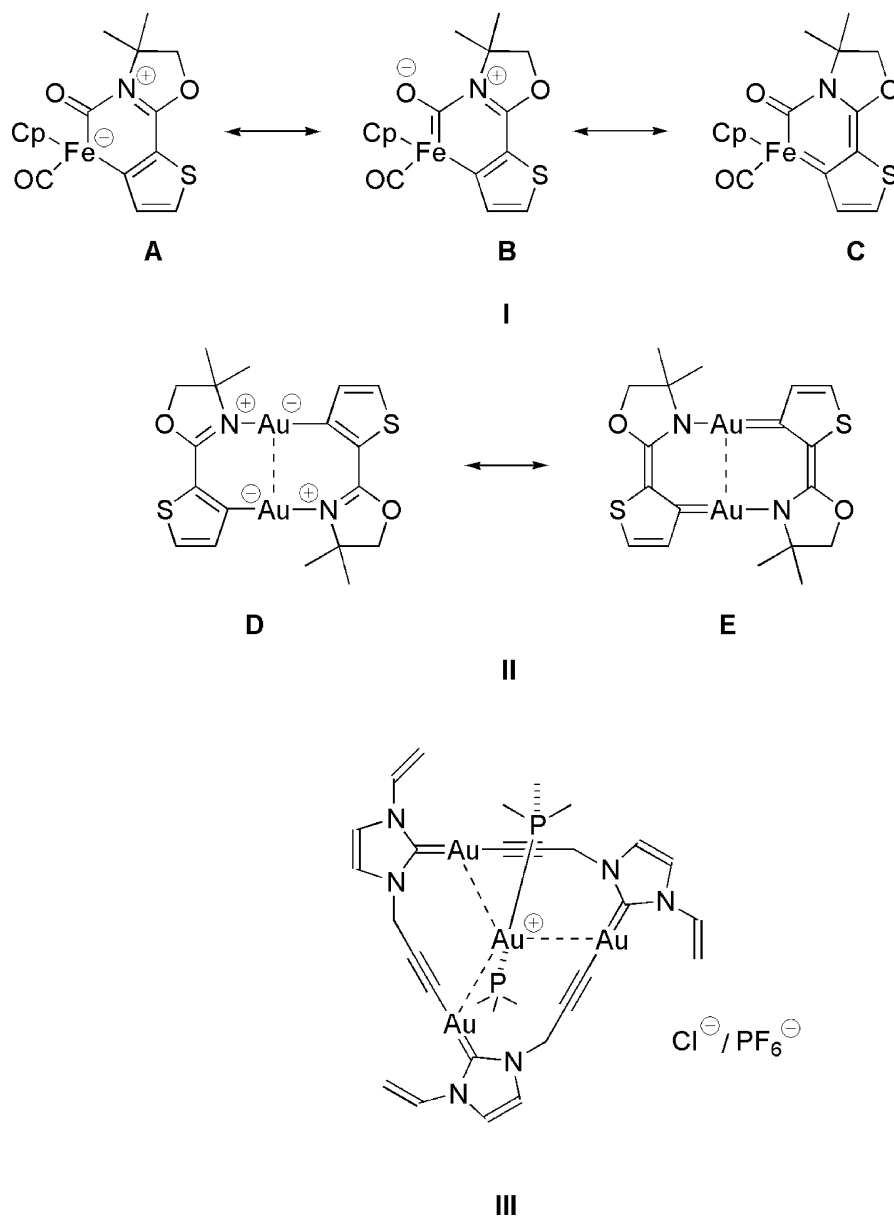


Fig. 1. Heterometallacyclic complexes previously prepared in our group using *exo*-bidentate ligands.

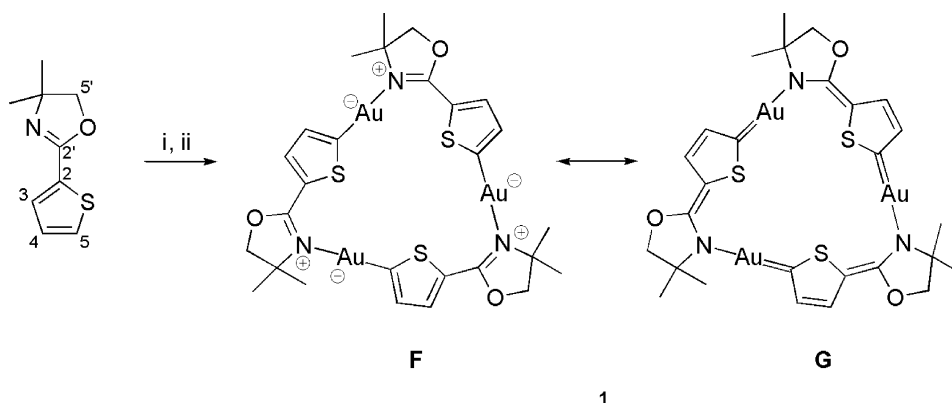
uct; iii) discuss the structure and bonding within the molecular framework of the latter in terms of its most important resonance structures.

Results and Discussion

Synthetic considerations

Upon selective deprotonation of 4,4-dimethyl-2-(thien-2-yl) oxazoline with lithium diisopropyl-

amide (LDA) at -80°C [10, 11] and subsequent reaction with $[\text{AuCl}(\text{THT})]$ dissolved in tetrahydrofuran (THF), the solution turned slightly yellow, and a cyclic, trimeric compound (**1**) was formed (Scheme 1). The product ran on a TLC plate with methylene chloride as eluant, indicating its neutrality. Colorless crystals, **1a**, containing THF molecules were obtained; the solvent molecules could be removed under vacuum, but the crystals



Scheme 1. i) LDA; ii) [AuCl(THT)].

turned dull once out of contact with the mother liquor.

The ^{13}C NMR signal of C-5 of the coordinated thiophene ring (see Scheme 1) is found 38.8 ppm downfield from the corresponding signal ($\delta = 126.5$) in the starting compound. Despite the decreased carbon shielding upon coordination, only a relatively small contribution of the resonance structure **G** is indicated – even compared to the situation in an isolobal pentacarbonyltungsten(0) thienylidene with coordination at C-5 ($\Delta\delta = 73.5$) [3] and in a corresponding phosphinegold(I) carbene complex, albeit with the metal then positioned at C-3 of the thienyl oxazoline ($\Delta\delta = 61.4$) [4]. This evidence of the predominance of the mesomeric structure **F** was complemented by the crystal structure determinations described below.

Electrospray ionization mass spectrometry of solvated **1** exhibited no m/z value corresponding to the molecular ion, but a homoleptic cation $[\text{AuL}_2]^+$ (L represents the neutral thienyl oxazoline, *e. g.* the protonated ligand) was observed as the base peak at $m/z = 559$.

Encouraged by the above-mentioned result in which a $[\text{Au}(\text{PMe}_3)_2]^+$ complex cation is trapped in the center of an 18-membered gold-containing ring by aurophilic interactions [5], the incorporation of linear chloro(*t*-butylisocyanide)gold(I) within cyclic **1** was investigated. No reaction was observed but, interestingly, crystals of a second THF solvate, **1b**, were recovered from the reaction mixture. The failure to react could be ascribed to the inhibitingly strong intramolecular $\text{Au}\cdots\text{S}$ contacts, which effectively form a smaller ring within the larger 18-membered metallacycle (see Fig. 2, and Supporting Information, Fig. S1),

placing structural restraints on the hosting of the linear gold complex. Such a simple interpretation implies that from a thermodynamic viewpoint, the stabilizing influence of the potential three new intermolecular $\text{Au}\cdots\text{Au}$ interactions is less than that accomplished by the existing six intramolecular $\text{Au}\cdots\text{S}$ contacts.

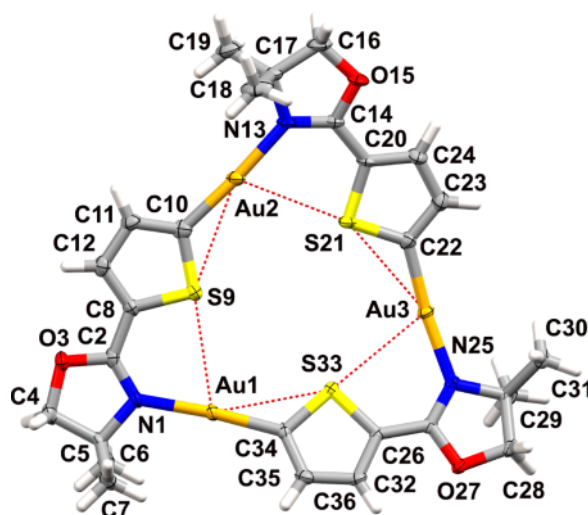


Fig. 2. (color online). Molecular structure and numbering system of the trinuclear gold complexes **1a** and **1b** (shown here is **1a** with displacement ellipsoids drawn at the 50% probability level). Selected bond lengths (Å) and angles (deg): (**1a**) Au1–C34 1.986(5), Au1–N1 2.060(4), Au2–C10 1.991(6), Au2–N13 2.059(4), Au3–C22 1.984(5), Au3–N25 2.050(4); C34–Au1–N1 175.12(18), C10–Au2–N13 175.32(19), C22–Au3–N25 172.06(19); (**1b**) Au1–C34 1.979(7), Au1–N1 2.042(5), Au2–C10 1.986(6), Au2–N13 2.051(5), Au3–C22 1.985(6), Au3–N25 2.050(5); C34–Au1–N1 174.7(2), C10–Au2–N13 174.1(2), C22–Au3–N25 174.4(3).

Crystal and molecular structures

The two solvates of **1** crystallized in different crystallographic systems, namely **1a** in the monoclinic space group $C2/c$, and **1b** in the centrosymmetric triclinic space group $P\bar{1}$. Both of them consist of one molecule of a cyclic gold(I) complex and one (**1a**) or two (**1b**) molecules of THF accommodated in the asymmetric unit, respectively. The trinuclear gold complex shows a somewhat distorted linear geometry at all the metal atoms by the coordinating carbons from the thiophene rings and the imine N atoms from the oxazoline rings of three distinct bridging ligands (Fig. 2, [12]).

The trinuclear cyclic entity is stabilized by intramolecular $Au\cdots S$ contacts with separations ranging from *ca.* 3.26 up to 3.28 Å for **1a** and from 3.25 to 3.34 Å for **1b** (with the shortest $Au2\cdots S21 = 3.245(2)$ Å and the longest $Au1\cdots S9 = 3.339(2)$ Å). These interactions are somewhat stronger than those observed for a monomeric gold(I) complex with a tribenzothiazolyl phosphine ligand (3.34–3.46 Å) [13] or the intermolecular $Au\cdots S$ contacts responsible for the packing in discrete, bimetallic dithiocarboxylato complexes of Au(I) (3.43–3.58 Å) [14].

A comparison of the bond lengths in the metal complexes **1a** and **1b** with relevant examples from literature [3] clearly indicates the dominance of the mesomeric form **F** (Scheme 1). It also accentuates the negligible role played by the oxonium form which, for example, contributes more significantly

in *trans*-chlorobis(triphenylphosphine)[(3,4,4-trimethyl-1,3-oxazolidin-2-ylidene)-2(5H)-thien-(3H)-ylidene]palladium(II) triflate [3] and is then reflected in a shorter C–O distance of *ca.* 1.32 Å (here, on average, 1.35 Å).

The cyclic metal complex adopts slightly different conformations in **1a** and **1b** considering the orientation of the heterocyclic ligands towards the mean plane of the 18-membered metallacycle (Fig. 3). The greatest deviations with respect to this plane in **1a** are noticeable for the S33 thiophene ring as well as the O27 and O15 oxazoline rings with corresponding angles of $23.3(2)^\circ$, $21.2(2)^\circ$ and $13.4(3)^\circ$, and for the S9, S33 and S21 thiophene rings in **1b** with angles of $23.0(2)^\circ$, $22.4(2)^\circ$ and $20.1(3)^\circ$ (the remaining rings do not deviate more than 8°). The oxazoline rings themselves deviate from planarity by *ca.* 0.10 Å (O27) to 0.05 Å (O3) in **1a** and from 0.08 Å (O27) to 0.09 Å (O15) in **1b**.

The tilting of the heterocyclic rings as well as related differences in the conformation of the metallacycles in **1a** and **1b** can be ascribed to differences in weak intermolecular interactions, though it is worth noting that the geometrical parameters for the coordination at the metal centers in **1a** and **1b** remain more or less constant.

A striking feature in the crystal structure of **1a** is the presence of channels expanding along the crystal-

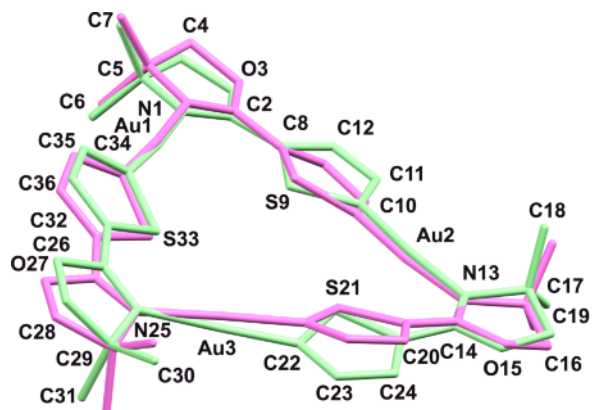


Fig. 3. (color online). Overlay of the trinuclear gold complexes in **1a** (green) and **1b** (pink) reflecting the changes in the ring conformation [15].

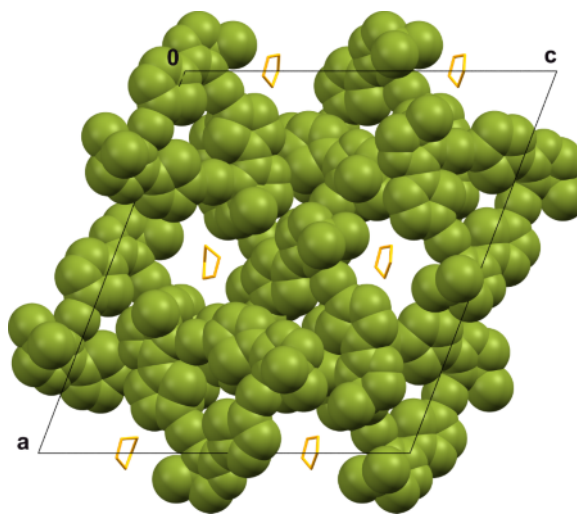


Fig. 4. (color online). Packing diagram of the molecules in **1a** shown down the *b* axis. Solvent occupying the channels is shown in capped-stick representation (only one molecule of THF shown for clarity; disorder and H atoms omitted); space-filling representation of the metal complexes.

lographic *b* axis (Fig. 4). The resulting assembly of the molecules could be classified in the host-guest category with a supramolecular 3D framework formed exclusively by means of weak C–H···O and C–H···S interactions between the metal complexes involving all the available O and S atoms of the heterocyclic ligands [16]. These open channels are occupied by disordered THF molecules that are stacked one above the other and interacting weakly through their O atoms with the host (C–H···O contacts).

In the crystal structure of **1b**, three different types of weak forces are present, namely once again weak C–H···O and C–H···S hydrogen bonding, but now supplemented by weak aurophilic interactions. The latter ($\text{Au1} \cdots \text{Au1}^i = 3.520(1) \text{ \AA}$, symmetry code *i*: $1 - x, -y, 1 - z$; and $\text{Au3} \cdots \text{Au3}^{ii} = 3.514(1) \text{ \AA}$, symmetry code *ii*: $1 - x, -y, 2 - z$) are found at the borderline of the cut-off distance for aurophilic interactions [17]. In the crystal structures of $[\text{AuCl}(\text{PEt}_3)]$ [18] or $[\text{AuCl}(\text{trithiane})]$ [19] even longer distances for aurophilic interactions with corresponding values of 3.568/3.615 and 3.558 Å have been observed, leading to an assembly of the molecules into chains comparable to our example (Fig. 5)

The weak hydrogen bonding involves all O and S atoms from the ligands. The THF molecules are located in the apertures extending along the crystallographic *c* axis of the 3D supramolecular assembly. The space here is limited by the protruding methyl groups of the oxazole rings, thereby influencing the positional freedom of the solvent molecules (Fig. 6). Furthermore, the THF molecules interact weakly with the host by C–H···O hydrogen bonding in which the molecule that contains O37 is involved as donor as well as acceptor whereas, in another solvent molecule, O42 acts only as an electron pair donor as reflected in

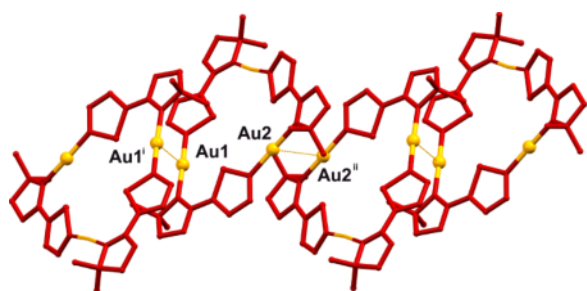


Fig. 5. (color online). Fragment of the chain in **1b** formed by aurophilic interactions with the atoms involved shown as balls.

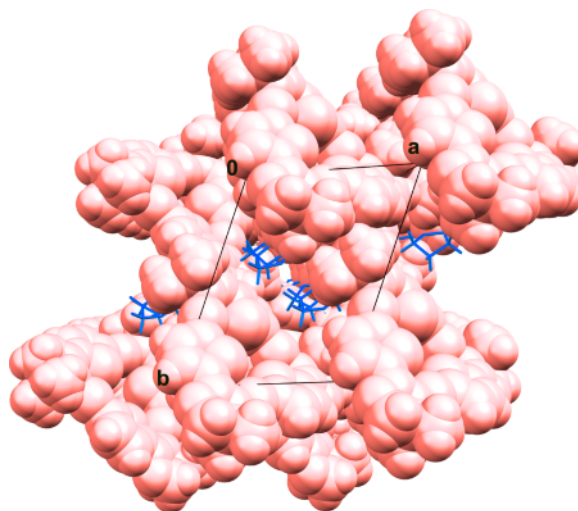


Fig. 6. (color online). Packing diagram of **1b** shown down the *c* axis; metal complexes are shown in space-filling representation, solvent as capped-sticks.

the larger atomic displacement parameters for the latter THF molecule.

Conclusions

In certain polynuclear gold heterometallacycles, well-positioned S atoms interact with the gold centers and thus determine the ligand orientations as well as the reactivity of the complex. Included solvent molecules, in our examples, stabilize the crystalline phase, but also have the ability to modify it when present in varying molar ratios. The outcome is the formation of different supramolecular assemblies organized by weak hydrogen bonds as well as aurophilic interactions (in one example).

Experimental Section

All reactions and manipulations were conducted under an atmosphere of dry argon using standard Schlenk and vacuum line techniques. Solvents were freshly distilled under a dry argon atmosphere before use: CH_2Cl_2 from CaH_2 , pentane and hexane from sodium, Et_2O and THF from sodium wire in the presence of sodium benzophenone ketyl radical. Diisopropylamine was distilled from and stored on a 3 Å molecular sieve. Other commercial chemicals were used as supplied. The reagents 4,4-dimethyl-2-(thien-2-yl) oxazoline [10] and $[\text{AuCl}(\text{THT})]$ [20] were prepared according to literature procedures. Butyllithium in hexane was standardized following the procedure of Winkle *et al.* [21].

	1a	1b
Formula	C ₂₇ H ₃₀ Au ₃ N ₃ O ₃ S ₃ ·C ₄ H ₈ O	C ₂₇ H ₃₀ Au ₃ N ₃ O ₃ S ₃ ·2(C ₄ H ₈ O)
<i>M_r</i>	1203.72	1275.83
Crystal shape	block	plate
Crystal size, mm ³	0.41 × 0.34 × 0.30	0.21 × 0.20 × 0.09
Temperature, K	100(2)	100(2)
Crystal system	monoclinic	triclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> , Å	28.722(6)	10.899(4)
<i>b</i> , Å	10.001(2)	13.935(5)
<i>c</i> , Å	26.062(5)	14.081(5)
α , deg	90	90.843(6)
β , deg	110.98(3)	103.430(6)
γ , deg	90	110.770(5)
<i>V</i> , Å ³	6990(3)	1933(1)
<i>Z</i>	8	2
<i>D</i> _{calcd} , g cm ^{−3}	2.29	2.19
μ (MoK α), cm ^{−1}	127.8	115.6
<i>F</i> (000), e	4496	1204
<i>hkl</i> range	−35 ≤ <i>h</i> ≤ 22 −11 ≤ <i>k</i> ≤ 12 −30 ≤ <i>l</i> ≤ 32	−13 ≤ <i>h</i> ≤ 13 −17 ≤ <i>k</i> ≤ 17 −17 ≤ <i>l</i> ≤ 17
((sin θ)/ λ) _{max} , Å ^{−1}	0.6252	0.6309
Refl. measured	19860	21105
Refl. unique	7068	8007
<i>R</i> _{int}	0.0291	0.0313
Param. refined	444	458
<i>R</i> (<i>F</i>)/ <i>wR</i> (<i>F</i> ²) ^a (all refl.)	0.0300/0.0595	0.0421/0.0799
<i>R</i> (<i>F</i>)/ <i>wR</i> (<i>F</i> ²) ^a [<i>I</i> > 2 σ (<i>I</i>)]	0.0269/0.0585	0.0344/0.0770
GoF (<i>F</i> ²) ^b	1.117	1.059
$\Delta\rho_{\text{fin}}$ (max/min), e Å ^{−3}	1.574/−0.926	2.935/−1.374

Table 1. Crystal structure data for **1a** and **1b**.

^a $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^b GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

¹H and ¹³C NMR spectra were recorded on a Varian Unity Inova 400 spectrometer at respectively 400 and 75.4 MHz; δ values were referenced relative to residual solvent peaks. ESI mass spectra were recorded on a Waters API Quattro Micro instrument at 15–50 V cone voltage.

Cyclo-tris[$\{\mu$ -4,4-dimethyl-2-(thien-2-yl)(κ C⁵)oxazoline- κ N}gold(I)] (**1**)

A 10 mL solution of LDA (*ca.* 0.55 mmol) prepared from diisopropylamine (0.072 g, 0.71 mmol) and *n*-BuLi in hexane (0.92 mL, 1.3 M, 0.55 mmol) was added drop by drop to a solution of the thienyl oxazoline (0.098 g, 0.54 mmol) in THF at −78 °C. After 30 min, [AuCl(THT)] (0.17 g, 0.54 mmol) was slowly added, and the mixture stirred at this temperature for another hour before it was allowed to reach room temperature. The solvent was removed under vacuum, the residue carefully washed with ether and pentane and then recrystallized from CH₂Cl₂/pentane at −20 °C. The colorless crystals were filtered off and a few (**1a**) selected for single-crystal X-ray diffraction study. The rest were washed with cold pentane and stripped of solvent under vacuum.

Yield: 0.12 g, 61 %, decompos. p. 132 °C (with no melting). – ¹H NMR (CDCl₃): δ = 7.90 (d, 3H, ³*J* = 3.65 Hz, H⁴), 7.04 (d, 3H, *J* = 3.65 Hz, H³), 4.30 (s, 6H, H^{5'}), 1.56 (s, 18H, Me). – ¹³C NMR (CDCl₂): δ = 165.3/164.4 (C⁵/C^{2'}), 136.0/134.6 (C²/C³), 125.9 (C⁴), 79.7 (C^{4'}), 79.7 (C^{4'}), 67.8 (C^{5'}), 28.9 (Me). – MS (ESI): *m/z* = 559 [Au{4,4-dimethyl-2-(thien-2-yl)oxazoline}]⁺, 196 [4,4-dimethyl-2-(thien-2-yl)oxazoline]⁺. – C₂₇H₃₀N₃O₃S₃Au₃ (1131.64) (%): calcd. C 28.66, H 2.67, N 3.71; found C 28.40, H 2.59, N 3.55.

Compound **1** dissolved in THF did not react with an equimolar amount of [chloro(*t*-butyl)isocyanide]gold as indicated by NMR measurement of the residue of the reaction mixture in CDCl₃. Small, colorless crystals of **1b** formed in the NMR tube.

X-Ray structure determination

Single-crystal X-ray diffraction data were collected on a Bruker SMART Apex [22a] diffractometer with graphite-monochromatized MoK α radiation. The data reduction was performed using the program SAINT+ [22b].

The empirical absorption corrections were performed using SADABS [23]. The structures were solved by Direct Methods with SHELXS-97 [24] and refined by full-matrix least-squares methods based on F^2 using SHELXS-97 [24].

The program MERCURY [25] was used to prepare molecular graphic images. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were placed in calculated positions with displacement factors fixed at 1.2 times U_{eq} of the parent C atoms and 1.5 times U_{eq} for methyl groups. A summary of the data collection and structure refinement parameters is provided in Table 1. In complexes **1a** and **1b** geometrical and anisotropic displacement parameter restraints were applied to the THF molecules. The solvent molecules in **1a** were found to be disordered around a twofold axis.

CCDC 896702 and 896703 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Supporting information

A figure showing two 18-membered, gold-containing cyclic structures is available online (DOI: 10.5560/ZNB.2012-0222).

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