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Synthesis, properties and crystal structures of volatile dimethylgold(III) complexes based on phenyl-containing β -diketones and β -iminoketone

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ABSTRACT

We have synthesized and studied volatile dimethylgold(III) complexes based on phenyl-containing β -diketones and β -iminoketone, namely (CH₃)₂Au(C₆H₅-CO-CH-CO-CH₃), (CH₃)₂Au(bac) (**1**); (CH₃)₂Au (C₆H₅-CO-CH-CO-CH₃), (CH₃)₂Au(bac) (**1**); (CH₃)₂Au (C₆H₅-CO-CH-CO-CH₃), (CH₃)₂Au(btfa) (**2**); and (CH₃)₂Au(C₆H₅-CO-CH-C(NH)-CH₃), (CH₃)₂Au(i-bac) (**3**). The obtained compounds were identified by elemental analysis, ¹H NMR and IR-spectroscopy, and were characterized by DTA and single-crystal X-ray diffraction studies. In compounds **2** and **3**, the Au atom has a square coordination environment AuC₂O₂ and AuC₂NO, respectively.

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1. Introduction

Current interest is growing in gold-containing films and nanoparticles, which may be used extensively in microelectronics and catalysis [1-4]. One method to produce materials with specified functional properties is metal-organic chemical vapor deposition (MOCVD), using volatile metal-organic compounds. This method allows gold to be deposited as minute particles [5] or films of various thickness, structure and morphology [6-9]. The deposition of gold on the surface of solids with a highly developed surface is an important method for preparing catalyzers with highly dispersed active components and is of great interest to solve the advanced problems in practical catalysis [10]. A lack of adequate precursors, however, restricts the study of gold processes by MOCVD [3]. Compounds used in CVD processes must be capable of satisfying several requirements: pronounced vapor pressure at low temperatures, high thermal stability in condensed and gaseous states, non-toxicity, moisture resistance and long shelf life.

Literature data show that of the few known volatile gold compounds, dimethylgold(III) complexes with β -diketones [11–14] have particular features to be the most suitable for use in gaseous processes. Those compounds show a wide range of variation in volatility and thermal stability in the condensed and gaseous states, depending on terminal substituents and on the type of donor atoms in the ligand [15]. A topical problem is the synthesis and a study of the thermal behavior and structural features, as well as the correlation between the composition, the crystal structure and the properties of compounds which may be used as gold precursors in CVD processes.

We have previously performed complex research on β -diketonates and β-iminoketonates of dimethylgold(III) with various alkyl and trifluoroalkyl substituents in the ligand. The syntheses conditions, properties, structures [16-18] and thermal characteristics of these complexes in the condensed and gaseous states [11,15] were studied. To continue investigations of volatile gold-(III) compounds we have studied volatile dimethylgold(III) complexes based on phenyl-containing ligands, such as (CH₃)₂Au $(C_6H_5-CO-CH-CO-CH_3)$, $(CH_3)_2Au(bac)$ (1); $(CH_3)_2Au(C_6H_5-CO-CH_3)$ CH-CO-CF₃), $(CH_3)_2Au(btfa)$ (2); and $(CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH_3)_2Au(C_6H_5-CO-CH-CH_3)_2Au(C_6H_5-CO-CH_3)_2Au(C_6H_5-CO-CH_3)_2Au(C_6H_5-CO-CH_5-CO-CH_5-CH_5)_2Au(C_6H_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5)_2Au(C_6H_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5)_2Au(C_6H_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO-CH_5-CO$ $C(NH)-CH_3$, $(CH_3)_2Au(i-bac)$ (3). Complex 1 alone is reported in literature [19], which was obtained by the exchange reaction between dimethylgold iodide and the Tl(bac) salt. Complexes 2 and **3** were first prepared and studied by the authors of this work. Data on the structure of complexes 1-3 have not previously been reported in the Cambridge Structural Database.

This paper reports the synthesis of **1–3**, data on elemental analysis, IR and ¹H NMR spectra and thermal analysis of the complexes by the DTA method. The structures of the complexes $(CH_3)_2Au(bt-fa)$ (**2**) and $(CH_3)_2Au(i-bac)$ (**3**) were determined. We failed to prepare a single crystal of $(CH_3)_2Au(bac)$ (**1**) suitable for structural X-ray study.





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2. Results and discussion

2.1. Synthesis and characterization of $(CH_3)_2Au(C_6H_5-CO-CH-CO-CH_3)$ (**1**), $(CH_3)_2Au(C_6H_5-CO-CH-CO-CF_3)$ (**2**) and $(CH_3)_2Au(C_6H_5-CO-CH-CO-CF_3)$ (**3**)

Dimethylgold(III) iodide, $[(CH_3)_2AuI]_2$, was used as the starting compound for the synthesis of the volatile gold(III) β -diketonates and β -iminoketonate. This complex was previously prepared from AuCl₃Py and CH₃MgI with 21% [20] and 35% [21] yields. We have developed a new method for the synthesis from KAuCl₄ with a 55% yield. The structure of the complex $[(CH_3)_2AuI]_2$ was first studied by us [22].

To synthesize dimethylgold chelates, we have used the ligands 1-phenyl-1,3-butane dione, $C_6H_5COCH_2COCH_3$ (Hbac); 1,1,1-tri-fluoro-4-phenyl-2,4-butanedione, $C_6H_5COCH_2COCF_3$ (Hbtfa); and 1-phenyl-3-amino-2-butene-1-one, $C_6H_5COCHC(NH_2)-CH_3$ (Hibac).

Complexes $(CH_3)_2Au(bac)(1)$ and $(CH_3)_2Au(i-bac)(3)$ were prepared by the reaction between $[(CH_3)_2Aul]_2$ and the ligand potassium salts. Chloroform and ethanol in a 5:1 ratio were used as solvents. The fluorinated complex $(CH_3)_2Au(btfa)(2)$ was prepared by the reaction of the dimethylgold iodide and the ligand in heptane in the presence of the silver oxide (Ag_2O) . The compounds prepared are white low-fusible crystalline substances. These may be stored for long periods of time at temperatures below zero and are readily soluble in organic solvents.

In the IR spectra of the complexes over the $1530-1600 \text{ cm}^{-1}$ range there are intense absorption bands of the C–O vibration, confirming the chelate type of bonding between the gold atom and the ligand. In the spectrum of **3** there is a strong typical wide band at about 3350 cm^{-1} , due to valent v(N-H) vibrations [23]. In the ¹H NMR spectra of complexes **1** and **3**, the protons of the CH₃ groups immediately bonded to the gold atoms appear as two signals with a 1:1 intensity relation, independent of the type of the donor atoms of the chelation mode. These data and elemental analysis results confirm the successful preparation of complexes **1–3**.

2.2. Structural characterization of 2 and 3

An X-ray structural study revealed that the structure of compound **2** belongs to the molecular type and is built of neutral (CH₃)₂Au(btfa) complexes. The structure and the atomic numbering scheme are shown in Fig. 1a. The gold atom is coordinated to two oxygen atoms of the β -diketonate ligand and two carbon atoms of the methyl groups; the coordination environment is a slightly distorted AuC₂O₂ square. The Au–O distances are 2.112 Å, the average Au-CH₃ bond value is 2.014 Å and the chelate O-Au-O bond angle is 89.4°. In the ligand, the O-C bonds are equal, the difference in C–C $_{\gamma}$ and C–C $_{Me}$ bonds on the side of different substituents is 0.02 Å and the average C-C and C-F bond values in the substituents are 1.39 and 1.33 Å, respectively. The small bending of the metal cycle along the O···O line is 3°. The phenyl ligand ring is turned by 9.4° to the coordination square plane and the torsion C(5)C(4)C(3)F(3) angle is 26.5°. A general view of the crystal structure is shown in Fig. 2a. The gold atom coordination is supplemented to a pyramidal (4 + 1) coordination with the H_v atom of the neighboring complex with a Au \cdots H separation of 3.42 Å to form dimeric associates with a Au…Au separation of 5.859 Å (Fig. 3a), the remaining Au. Au separations being >7.15 Å. In the crystal the shortest intermolecular $F \cdots F$ and $F \cdots H$ separations are 2.99 and 2.80 Å, respectively.

The structure of compound **3** is of the molecular type and comprises of neutral $(CH_3)_2Au(i-bac)$ complexes. The structure is shown along with the atomic numbering scheme in Fig. 1b. The gold atom is coordinated to the oxygen and nitrogen atoms of the β -iminoketonate ligand and two carbons of the methyl groups to form a slightly distorted square. The Au–O distance is 0.045 Å longer than the Au–N distance, the average Au–CH₃ bond length is 2.038 Å, and the chelate bond O-Au-N angle is 90.5°. In the ligand, the O-C and N-C bonds are equal to within 0.01 Å, the difference in the $C-C_{\gamma}$ and $C-C_{Me}$ bonds on the side of different substituents is 0.05 and 0.02 Å, respectively. The significant difference in the C–C_{γ} bond lengths, 0.049 Å (that is >3 σ), may be likely explained by a certain loss of delocalization on the side of the methyl substituent. The average C-C bond value is 1.39 Å in the phenyl substituent. The bending of the chelate ring along the $O \cdots N$ line is negligible (1°). The phenyl ring plane is turned by 30.1° to the coordination square plane. In the structure, the molecules of the complexes are packed into infinite zig-zag stacks along the x-axis. A general view of the structure is shown in Fig. 2b. The gold atom coordination is supplemented to a bipvramidal (4 + 1 + 1) coordination with weak contacts to the C_v atom and to the phenyl ring hydrogen atom of the neighboring complexes, the Au \cdots C $_{\gamma}$ and Au \cdots H distances being 3.52 and 3.35 Å, respectively. In the stack, the Au Au separations are 5.091 and 6.118 Å, and the Au–Au–Au angle is 77.6° (Fig. 3b). The distances between the centers of the stacks are >10.5 Å and the shortest intermolecular H...H separation is 2.32 Å.

A comparison of the geometric characteristics of the studied dimethylgold(III) complexes based on a phenyl-containing β -diketone and β -iminoketone (**2** and **3**) with those obtained by us before for analogous complexes with various alkyl and trifluoroalkyl substituents in the ligand [16–18] showed that these values are close and the bond lengths are within the same ranges: Au–C (2.008–2.050 Å), Au–O (2.070–2.112 Å) and Au–N (2.051–2.091 Å).

2.3. Thermal study (DTA) of $(CH_3)_2Au(C_6H_5-CO-CH-CO-CH_3)$ (1), $(CH_3)_2Au(C_6H_5-CO-CH-CO-CF_3)$ (2) and $(CH_3)_2Au(C_6H_5-CO-CH-C(NH)-CH_3)$ (3)

The thermal study results are listed in Table 1. Upon heating under both helium and hydrogen atmospheres, the complexes behave alike. The DTA curves show the melting and decomposition effects in the complexes. Under inert conditions, complex 1 begins to decompose at 150 °C, while the fluorinated complex 2 decomposes at a significantly lower temperature. Replacing one oxygen atom by an NH group in the ligand causes the thermal stability of complex **3** to increase significantly. Upon heating the complexes in a hydrogen flow, their decomposition point is negligibly lower and the thermal stability changes with the ligand structure in a similar manner as under an inert atmosphere. This confirms the fact of the considerable inertness of dimethylgold β-diketonates to hydrogen as compared to β-diketonates of platinum group metals, whose thermal stability sharply decreases under a reducing medium [16]. Among the established regularities of changing the thermal stability of dimethylgold(III) chelates depending on the β-diketonate ligand structures, one can note good thermal characteristics of the β -iminoketonate complex **3**. This may be desirable for CVD processes to obtain gold film covers.

3. Concluding remarks

We have synthesized and studied volatile dimethylgold(III) complexes based on phenyl-containing β -diketones and β -iminoketone. An improved method for the synthesis of the original [(CH₃)₂AuI]₂ complex was suggested. A single-crystal X-ray diffraction study showed that the insertion of Ph and CF₃ substituents into the ligand virtually has no influence on the coordination environment of the Au atom in these complexes. The results obtained



Fig. 1. ORTEP drawing of (CH₃)₂Au(btfa) (2) (a) and (CH₃)₂Au(i-bac) (3) (b).

by the DTA method revealed that the replacement of one oxygen atom by an NH group results in a significant increase in the thermal stability of the β -iminoketonate (CH₃)₂Au(i-bac) (**3**) in both inert (Ar) and reduced (H₂) atmospheres. In accordance with its thermal characteristics, this complex may be used as a precursor in CVD processes.

4. Experimental

4.1. General considerations

The starting complex, dimethylgold(III) iodide, was prepared from KAuCl₄, synthesized in its turn from hydrogen tetrachloroaurate(III) hydrate (Au, 99.9%). Compounds $(CH_3)_2Au(bac)$ (1),

 $(CH_3)_2Au(btfa)$ (**2**) and $(CH_3)_2Au(i-bac)$ (**3**) were purified by vacuum sublimation in a gradient tube oven ($P \sim 10^{-2}$ Torr, T = 50-250 °C). Elemental analysis was performed with a Carlo-Erba 1106 (Italy) device. Infrared spectra were measured in KBr pellets with the use of a Scimitar FTS2000 spectrometer. ¹H NMR spectra were recorded on a Bruker MSL300 spectrometer (300 MHz, 25 °C, ppm) with CDCL₃ as the solvent, and chemical shifts were referenced to the proton impurity of the NMR solvent (¹H). The thermal analysis was performed on a Q-1000 Derivatograph (MOM) in open standard crucibles, in both He and H₂ flows (110–120 ml/min), at a heating rate of 5 K/min and with samples of about 20 mg. Melting points were determined by a Kofler M.p. apparatus.

X-ray intensity data were collected on a Bruker X8Apex CCD diffractometer using standard techniques (ω - and φ -scans of narrow frames) at low temperatures and corrected for absorption effects



а

Fig. 2. Projection of the crystal packing of compounds 2 (a) and 3 (b).



Fig. 3. The additional coordination of the gold atom in the structure of 2 (a) and 3 (b).

Table 1		
Results of differential	thermal analysis	of the complexes.

Compound	M.p.(°C)	Decomp. star	Decomp. starting (°C)	
	DTA/He	DTA/He	DTA/H ₂	
$(CH_3)_2Au(bac)$ (1) $(CH_3)_2Au(btfa)$ (2) $(CH_3)_2Au(i-bac)$ (3)	46 66 57	150 80 200	140 75 165	

(SADABS). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX97 program set (Bruker AXS Inc., 2004) [24]. Crystallographic data and details of single-crystal diffraction experiments for compounds 1-3 are given in Table 2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms $H\gamma$ and H_{NH} were located from a difference map and were included in the refinement. The hydrogen atoms of the CH₃ groups were calculated by geometrical methods. Selected bond lengths and angles are in Table 3.

4.2. Synthesis of complex [(CH₃)₂AuI]₂

The Grignard reagent CH₃MgI was prepared from magnesium powder (0.25 g, 10.6 mmol) and iodine methyl (1.51 g, 10.6 mmol) in 30 ml of absolute diethyl ether, with further addition of 60 ml hexane, and then the solution was cooled to -30 °C. Dried KAuCl₄ salt (1.00 g, 2.65 mmol) was sprinkled onto the cooled solution

Table 1	2
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Crystal data and structure refinement for **2** and **3**.

Empirical formula	$C_{12}H_{12}AuF_{3}O_{2}(2)$	C ₁₂ H ₁₆ AuNO (3)
Formula weight	44 218	387.22
Temperature (K)	150(2)	100(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	P21/c
Unit cell dimensions		
a (Å)	8.4281(5)	7.0700(6)
b (Å)	11.1703(7)	16.0641(16)
<i>c</i> (Å)	13.8825(8)	10.8052(11)
β (°)	104.875(2)	105.682(2)
Volume (Å ³)	1263.16(13)	1181.5(2)
Ζ	4	4
D_{calc} (g/cm ³)	2.325	2.177
Absorption coefficient (mm ⁻¹)	11.674	12.425
F(000)	824	728
θ range for data collection	2.37-28.28	2.33-27.48
Index ranges	$-9 \leqslant h \leqslant 11, -14 \leqslant k \leqslant 14, -14 \leqslant l \leqslant 18$	$-8\leqslant h\leqslant 4$, $-20\leqslant k\leqslant 20$, $-13\leqslant l\leqslant 14$
Reflections collected	9019	8050
Independent reflections	2943 [<i>R</i> _{int} = 0.0377]	2649 $[R_{int} = 0.0305]$
Completeness to θ = 25.00° (%)	94.1	98.1
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data/restraints/parameters	2943/0/165	2649/0/147
Goodness-of-fit on F ²	1.121	0.954
Final R indices $[I>2\sigma(I)]$	$R_1 = 0.0321, wR_2 = 0.0750$	$R_1 = 0.0246, wR_2 = 0.0594$
R indices (all data)	$R_1 = 0.0476, wR_2 = 0.0783$	$R_1 = 0.0359, wR_2 = 0.0618$
Difference map (maximum, minimum, e Å $^{-3}$)	2.215/-1.798	2.391/-1.215

Ta	bl	e	3
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Selected bond lengths (Å) and angles (°) for 2 and 3.

Compound (2)			
Au(1)-C(2)	2.012(6)	C(2)-Au(1)-C(1)87.5(3)	87.5(3)
Au(1)-C(1)	2.016(6)	C(2) - Au(1) - O(1)	178.3(2)
Au(1)-O(1)	2.112(4)	C(1)-Au(1)-O(1)	90.9(2)
Au(1)-O(2)	2.113(4)	C(2) - Au(1) - O(2)	92.2(2)
C(4) - O(2)	1.263(7)	C(1)-Au(1)-O(2)	179.4(3)
C(6) - O(1)	1.260(7)	O(1)-Au(1)-O(2)	89.42(16)
C(4) - C(5)	1.386(8)	O(2)-C(4)-C(5)	130.8(6)
C(4) - C(3)	1.533(9)	O(1)-C(6)-C(5)	125.6(5)
F(3) - C(3)	1.336(8)	C(4)-C(5)-C(6)	125.8(6)
F(1) - C(3)	1.329(7)	C(4)-O(2)-Au(1)	122.1(4)
F(2)-C(3)	1.334(9)	F(1)-C(3)-F(2)	107.8(6)
C(6) - C(5)	1.408(8)	F(1)-C(3)-F(3)	106.2(6)
C(6) - C(7)	1.509(7)	F(2)-C(3)-F(3)	106.5(6)
		F(1)-C(3)-C(4)	111.4(5)
		F(2)-C(3)-C(4)	110.4(6)
		F(3)-C(3)-C(4)	114.2(5)
		C(6)-O(1)-Au(1)	126.2(4)
Compound (3)			
Au(1)-C(11)	2.036(5)	C(11) - Au(1) - C(12)	88.9(2)
Au(1) - C(12)	2.040(5)	C(11) - Au(1) - N(1)	178.45(18)
Au(1) - N(1)	2.051(4)	C(12) - Au(1) - N(1)	92.7(2)
Au(1) - O(1)	2.096(3)	C(11) - Au(1) - O(1)	88.00(18)
O(1)-C(4)	1.293(6)	C(12) - Au(1) - O(1)	176.84(17)
N(1)-C(2)	1.303(7)	N(1)-Au(1)-O(1)	90.46(15)
C(4) - C(3)	1.376(7)	C(4) - O(1) - Au(1)	123.5(3)
C(4) - C(5)	1.490(6)	C(2)-N(1)-Au(1)	127.2(4)
C(2) - C(3)	1.425(7)	O(1)-C(4)-C(3)	127.4(4)
C(2) - C(1)	1.511(7)	N(1)-C(2)-C(3)	123.1(5)
		C(4)-C(3)-C(2)	128.3(5)

under an argon flow with vigorous stirring. The reaction mixture was stirred under an inert atmosphere -10 °C for 0.5 h, then the temperature was gradually elevated to room temperature. The complex was isolated from the reaction mixture with slightly acid-ified water with ice. The organic layer was separated and the water layer was extracted with hexane three times. The prepared compound was isolated by solvent evaporation with no heating. Yield 0.51 g (55%). The complex [(CH₃)₂Aul]₂ is a colorless substance, insoluble in water but readily soluble in organic solvents, and the M.p. is 95–96 °C (with decomposition).

4.3. Synthesis of $(CH_3)_2Au(C_6H_5-CO-CH-CO-CH_3)$ (1)

One gram (1.4 mmol) of $[(CH_3)_2AuI]_2$ was dissolved in 50 ml of chloroform and mixed with a solution of freshly prepared K(bacac) salt (2.8 mmol) in a minimal amount of ethyl alcohol. The mixture was stirred at room temperature for 1 h, the KI residue gradually dropping out from the solution. The solution was separated from the precipitated residue and the solvent was eliminated under reduced pressure. The isolated product was purified by sublimation under a reduced pressure. Yield 0.9 g (85%). *Anal.* Calc. for C₁₂H₁₅O₂Au: C, 37.11; H, 3.86. Found: C, 36.79; H, 3.91%. ¹H NMR (ppm): 1.22 [s, Au–Me], 1.27 [s, Au–Me], 2.17 [s 3H, CH₃–CO], 6.00 [s, 1H, CH], 7.3–8.0 [br, 5H, ArH]. IR (cm⁻¹): 2911 (m), 1590 (vs), 1558 (vs), 1518 (vs), 1487 (s), 1449 (s), 1389 (vs), 1357 (m), 1283 (m), 1218 (m), 1184 (m), 1111 (w), 1072 (w), 1027 (w), 1000 (w), 949 (m), 857 (w), 828 (w), 798 (m), 774 (s), 715 (s), 684 (s), 623 (s), 545 (w), 462 (w). M.p.: 44–46 °C.

4.4. Synthesis of $(CH_3)_2Au(C_6H_5-CO-CH-CO-CF_3)$ (2)

Three hundred milligrams (2.8 mmol) of H(btfa) and 0.32 g (1.4 mmol) of freshly prepared silver oxide (Ag₂O) were added to a solution of [(CH₃)₂Aul]₂ (1 g, 1.4 mmol) in 50 ml of hexane. The reaction mixture was vigorously stirred at room temperature for 30 min. The solution was separated from the precipitated AgI residue. Then isolation and purification of the complex were performed under the conditions reported above. Yield 1.2 g (92%). *Anal.* Calc. for C₁₂H₁₂F₃O₂Au: C, 32.58; H, 2.71; F, 12.89. Found: C, 32.34; H, 2.52; F, 13.21%. IR (cm⁻¹): 2917 (m), 1600 (vs), 1571 (vs), 1532 (s), 1488 (m), 1431 (m), 1316 (m), 1290 (vs), 1251 (m), 1188 (s), 1134 (s), 1066 (m), 997 (w), 937 (w), 771 (m), 696 (m), 659 (m), 586 (w), 536 (w), 444 (vw) 413 (vw). M.p.: 64–65 °C.

4.5. Synthesis of $(CH_3)_2Au(C_6H_5-CO-CH-C(NH)-CH_3)$ (**3**)

A solution of the ligand salt prepared from KOH (0.16 g, 2.8 mmol) and the H(i-bacac) ligand (0.45 g, 2.8 mmol) in 10 ml of ethanol was added to a solution of $[(CH_3)_2AuI]_2$ (1 g, 1.4 mmol) in 50 ml of chloroform. The reaction mixture was stirred for 0.5 h at 40–45 °C and the KI residue was gradually precipitated from

the solution. Then the solvent was eliminated under reduced pressure and the dry residue was extracted with hexane. The product separated was purified by sublimation in a gradient furnace under reduced pressure. Yield 0.9 g (80%). Anal. Calc. for C₁₂H₁₆NOAu: C, 37.21; H, 4.13; N, 3.61. Found: C, 37.45; H, 4.33; N, 3.78%. ¹H NMR (ppm): 0.92 [s, 3H, Au-Me], 0.93 [s, 3H,Au-Me], 2.06 [s 3H, CH₃-CO], 5.49 [s, 1H, CH], 6.52 [s, 1H, NH], 7.8-8.3 [br, 5H, ArH]. IR (cm⁻¹): 3350 (m), 2923 (s),2852 (m) 1600 (vs), 1527 (vs), 1457 (s), 1406 (m), 1237 (m), 1186 (m), 1072 (m), 1022 (m), 948 (w), 843 (vw), 792 (w), 758 (s), 684 (s), 647 (m), 550 (w), 464 (w), 429 (vw). M.p.: 56-58 °C.

Supplementary data

CCDC 749430 and 749411 contain the supplementary crystallographic data for **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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