

Gold(I) Carboxylates and Fluorocarboxylates

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Z. Naturforsch. 57 b, 605–609 (2002); received March 14, 2002

Gold(I) Complexes, Gold(I) Carboxylates, Pentafluoropropionate Complexes

(Triphenylphosphine)gold(I) pivalate (1), and (triphenylphosphine)gold(I), [tri(*p*-tolyl)-phosphine]gold(I), [(4-dimethylaminophenyl)diphenylphosphine]gold(I), and (cyclohexylisocyanide)gold(I) pentafluoropropionate (2–5) have been prepared from the corresponding gold(I) halide complexes and silver carboxylates in high yields. The products are stable to air and moisture and soluble in most common polar organic solvents. The structures of 1 and 3 have been determined. Owing to the bulk of the carboxylate substituents the molecules are monomers in the crystal. Compounds 1–4 undergo thermal decomposition in a narrow temperature range around 130 °C, 5 is less stable and decomposes at 48 °C.

Introduction

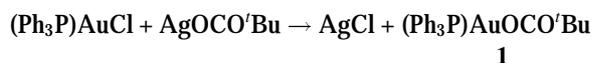
Gold(I) complexes of the type L-Au-X with a neutral and an anionic ligand (L/X) are of current interest owing to their fascinating structural chemistry and their potential for applications in a variety of technologies and in medicine [1]. Among the ligands L employed for tailoring the properties of the compounds the large family of tertiary phosphines and arsines are most prominent [1], but isonitriles have recently also gained considerable attention [2]. As for the anions X⁻, the heavier halides were most common counterions in the early fundamental studies, but most of the contemporary investigations have focussed on sulfides and selenides. By contrast, gold(I) fluorides [3] and gold(I) complexes with oxygen-bonded anionic components are still non-existent (F⁻) or rare (OR⁻) in gold(I) coordination chemistry [1].

In a search for compounds with highly electronegative oxygen-bonded groups X⁻ [4] we have studied a series of perfluorinated carboxylates and related compounds. Following an initial report published in 2000 [5] we now present complementary results obtained with perfluoropropionic acid. The complexes are expected to undergo "clean" decomposition to leave pure gold on a variety of substrates that find applications in microelectronics or in catalysis [6]. The synthesis and structure of a gold(I) pivalate complex is also reported as a refer-

ence compound with a non-fluorinated carboxylate group.

Preparative Results

Treatment of (triphenylphosphine)gold(I) chloride with silver pivalate ('butylcarboxylate) in the molar ratio 1:1 in dichloromethane at 20 °C affords the expected (triphenylphosphine)gold(I) pivalate (1) in 95% yield as a colourless crystalline solid, m. p. 132 °C (with decomposition).



Crystals grown from dichloromethane / pentane are stable in air and show no sign of decomposition in solution (tetrahydrofuran, chloroform, dichloromethane) at 20 °C. They are unaffected by water. The NMR spectra of solutions in chloroform feature the ¹H, ¹³C and ³¹P resonances suggested by the molecular formula. The elemental analysis is also in agreement with the calculated data, but the FAB mass spectrum shows a dinuclear cation {[(Ph₃P)₂Au₂]OCO'Bu}⁺ as the parent peak (7% rel. abundance).

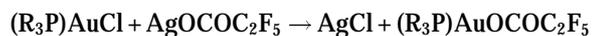
An analogous reaction of (Ph₃P)AuCl with silver pentafluoropropionate carried out at -70 °C gives (triphenylphosphine)gold(I) pentafluoropropionate (2) in 85% yield, m. p. 134 °C (with decomposition). The corresponding tri(*p*-tolyl)phosphine (3) and diphenyl-(*p*-dimethylamino-phenyl)phosphine

	1	3
<i>Crystal data</i>		
Formula	C ₂₃ H ₂₄ AuO ₂ P	C ₂₄ H ₂₁ AuF ₅ O ₂ P
M _r	560.36	664.34
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	12.5777(2)	13.0318(3)
<i>b</i> (Å)	13.4590(2)	11.6964(2)
<i>c</i> (Å)	14.4535(3)	15.6841(4)
α (°)	68.179(1)	90
β (°)	71.106(1)	100.601(1)
γ (°)	70.588(1)	90
<i>V</i> (Å ³)	2085.51(6)	2349.85(9)
ρ_{calc} (gcm ⁻³)	1.785	1.878
<i>Z</i>	4	4
<i>F</i> (000)	1088	1280
μ (Mo- <i>K</i> α) (cm ⁻¹)	71.85	63.87
<i>Data collection</i>		
<i>T</i> (K)	143	143
Measured reflections	47991	76807
Unique reflections	12617 [<i>R</i> _{int} = 0.046]	4951 [<i>R</i> _{int} = 0.059]
Absorption correction	DELABS	DELABS
<i>T</i> _{min} / <i>T</i> _{max}	0.511/0.845	0.188/0.658
<i>Refinement</i>		
Refined parameters	487	298
Final <i>R</i> values [<i>I</i> ≥ 2σ(<i>I</i>)]		
<i>R</i> 1	0.0359	0.0374
<i>wR</i> 2 ^[a]	0.0879	0.0836
(shift/error) _{max}	< 0.001	< 0.001
ρ_{fin} (max/min) (eÅ ⁻³)	1.502/-1.419	1.370/-1.059

Table 1. Crystal data, data collection, and structure refinement of compounds 1 and 3.

^[a] $wR2 = \{[\sum w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0368$ (1), 0.0373 (3); $b = 4.66$ (1), 7.09 (3).

complex (4) are obtained similarly in 95% and 98% yield, m. p. 138 °C / 132 °C (with decomposition), respectively.

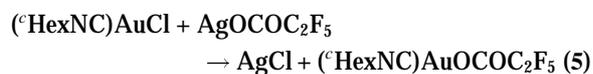


2: R = Ph, 3: R = *p*-Tol,
4: R₃ = Ph₂(4-Me₂N-C₆H₄)

All three products are stable to air and water at room temperature. Elemental analyses and solution NMR spectra confirm the expected composition and structure. In the mass spectra (FAB) the dinuclear cations $\{[(R_3P)Au]_2OCOC_2F_5\}^+$ represent the peaks of highest mass. Attempts to grow single crystals were only successful for complex 3.

(Cyclohexylisocyanide)gold(I) chloride was also found to give an analogous pentafluoropropionate complex (5, 90% yield, m. p. 48 °C with decomposition), but this product is of very limited stability and needs to be handled and stored at low temper-

ature to avoid decomposition both as a solid and in solution.



While compounds 1 - 4 are not sensitive to light, complex 5 requires careful protection of the reaction and storage vessels by aluminium foil. The compound has an infrared absorption (KBr) at 2253 cm⁻¹ assigned to the isocyanide stretching frequency. The parent ion in the FAB mass spectrum is $\{[^{c}\text{HexNC}Au]_2OCOC_2F_5\}^+$ in 100% rel. abundance.

Thermal decomposition of compounds 1 - 5 on solid substrates yields elemental gold with little contamination because of the excellent leaving group properties of the phosphines and isocyanide, and - in particular - of the perfluoropropionate groups. The resulting gold particles or thin films are under investigation for application in surface technology [1] and in heterogeneous catalysis [5].

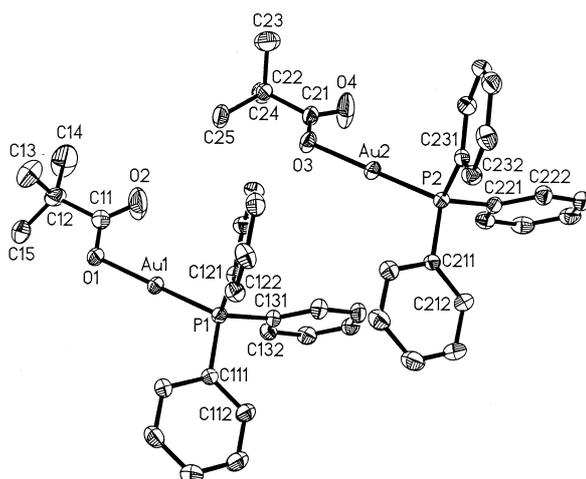


Fig. 1. The two independent molecules of the complex $(\text{Ph}_3\text{P})\text{AuOCO}'\text{Bu}$ (1) in the crystal with atomic numbering (ORTEP, 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Au1-O1 2.052(3), Au1-P1 2.217(1), Au2-O3 2.050(3), Au2-P2 2.214(1), O1-C11 1.280(5), O2-C11 1.188(6), O3-C21 1.276(5), O4-C21 1.212(6); O1-Au1-P1 173.03(9), O3-Au2-P2 171.82(9), Au1-O1-C11 117.7(3), Au2-O3-C21 117.4(3), O1-C11-O2 123.8(5), O3-C21-O4 125.0(4).

Structures

The crystal and molecular structures of compounds 1 and 3 have been determined by single crystal X-ray methods (Table 1).

Crystals of complex 1 (from dichloromethane / pentane at -30°C) are triclinic, space group $P\bar{1}$, with $Z = 4$ formula units in the unit cell. The asymmetric unit contains two independent monomers with very similar structures (Fig. 1). The bulk of the phosphine and pivalate ligands rules out any close approach of the monomers to allow aurophilic contacts between the metal atoms. The Au-O and Au-P distances are close to standard values available in the literature. The deviations of the P-Au-O angles from linearity by about 7° (Au1) and 8° (Au2) are probably also caused by packing forces between the large organic groups. The carbon-oxygen distances are different in each carboxylate group with the shorter values for the carbonyl part and the longer values for the gold-bound oxygen atoms Au-O-C. The angles Au-O-C in the two molecules are equal within the standard deviations (average 117.5°).

Crystals of complex 3 (from dichloromethane / pentane at -30°C) are monoclinic, space group $P2_1/n$, with $Z = 4$ formula units in the unit cell.

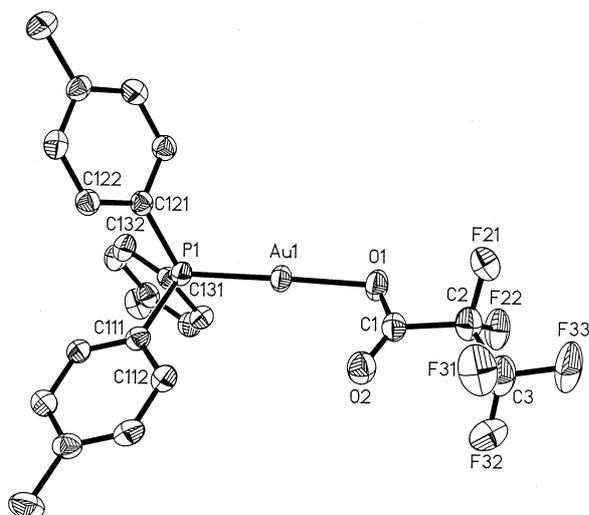


Fig. 2. The molecular structure of the complex $[(^p\text{Tol})_3\text{P}]\text{AuOCOC}_2\text{F}_5$ (3) with atomic numbering (ORTEP, 50% probability ellipsoids). Selected bond lengths [Å] and angles [°]: Au1-O1 2.069(4), Au1-P1 2.204(1), O1-C1 1.261(7), O2-C2 1.213(7); O1-Au1-P1 178.7(1), Au1-O1-C1 115.2(3), O1-C1-O2 129.8(5), O2-C1-C2 109.9(5), O2-C1-C2 120.2(5).

The asymmetric unit contains one molecule which has no unusually short contacts with neighbouring units (Fig. 2). The P-Au-O axis in this molecule is very close to linear [$178.7(1)^\circ$] with Au-P and Au-O bond lengths similar to those in 1 and other reference compounds. The Au-O-C angle is $115.2(3)^\circ$, only a little smaller than in 1. The C-O distances C1-O1 1.261(7) and C1-O2 1.213(7) Å differ by 0.048 Å, with the shorter bond again found for the carbonyl group. This difference is significantly less than for complex 1 with C11-O1 1.280(5), C11-O2 1.188(6), C21-O3 1.276(5), and C21-O4 1.212(6) Å and differences of 0.092 and 0.064 Å, respectively. It appears that the highly electronegative substituents in 3 lead to an equilibration of the C-O distances in the carboxylate group. The pentafluoropropionate groups have their fluorine and oxygen atoms in staggered conformations. The remainder parts of the compound (3) and the packing of the molecules show no irregularities. Selected data are given in the caption to Fig. 2.

Discussion

In the present study five compounds have been prepared with pivalate or perfluoropropionate

groups attached to two-coordinate gold(I) centers bearing either a tertiary phosphine or an isocyanide auxiliary ligand. These bulky carboxylate groups rule out any significant intermolecular interactions both in solution and in the solid state [1b]. The phosphine complexes are readily soluble in common organic solvents and decompose in the narrow range of 130 - 140 °C (1 - 4). The isocyanide complex is less stable and must be kept at low temperature in order to avoid decomposition. Owing to the low affinity of oxygen and fluorine for gold, the carboxylates have excellent leaving group properties which provide minimum contamination in the metal residue. For this reason compounds 1 - 4 are promising candidates for the controlled decomposition on surfaces to give gold thin films for heterogeneous catalysis [6] or other applications.

Experimental Section

Conventional equipment was used throughout. All experiments were carried out under an atmosphere of dry and pure nitrogen. Solvents were dried and distilled under nitrogen prior to use. Glassware was oven-dried and filled with nitrogen. The silver carboxylates were prepared from the corresponding carboxylic acids following literature procedures. The (phosphine)gold chlorides were generated from tetrachloroauric acid and the phosphines in a conventional redox reaction [7]. (^cHexylisocyanide)gold chloride was obtained by reaction of (tetrahydrothiophene) gold chloride with ^chexylisocyanide [8].

(Triphenylphosphine)gold pivalate (1)

A solution of Ph₃PAuCl (350 mg, 0.71 mmol) in dichloromethane (20 ml) is added to a suspension of ^tBuCOOAg (180 mg, 0.86 mmol) in the same volume of the same solvent at 20 °C with stirring and under protection against incandescent light. The mixture is stirred for 12 h and subsequently filtered, and the product precipitated from the filtrate by addition of pentane, collected by filtration and recrystallized from dichloromethane (376 mg, 95% yield), m. p. 132 °C (decomp.). NMR (CDCl₃, 20 °C), ¹H: 1.23, s, 9H, Me; 7.57 - 7.39, m, 15H, Ph. ¹³C{¹H}: 27.9, s, Me; 39.8, s, Me₃C; 128.3, d, *J* = 62.8 Hz, C(*ipso*); 128.6, d, *J* = 12.3 Hz, C(*meta*); 131.2, s, C(*para*); 133.7, d, *J* = 13.1 Hz, C(*ortho*); COO not detected. ³¹P{¹H}: 28.2, s. MS (FAB): *m/z* 1021, 7% [[(Ph₃P)Au]₂OCOCMe₃]⁺; 721, 32% [(Ph₃P)₂Au]⁺; 561, 3% [M]⁺; 459, 100% [Ph₃PAu]⁺. C₂₃H₂₄AuO₂P (560.36): calcd. C 49.3, H 4.3; found C 49.4, H 4.4.

(Triphenylphosphine)-, [tri(*p*-tolyl)phosphine]-, and [(4-dimethylaminophenyl)diphenylphosphine]-gold pentafluoropropionate (2 - 4)

The three compounds were obtained from the following reagents: 2: F₅C₂COOAg (200 mg, 0.74 mmol), (Ph₃P)AuCl (300 mg, 0.60 mmol); 3: F₅C₂COOAg (180 mg, 0.67 mmol), [(^pTol)₃P]AuCl (300 mg, 0.56 mmol); 4: F₅C₂COOAg (110 mg, 0.41 mmol), [(4-Me₂N-C₆H₄)Ph₂P]AuCl (200 mg, 0.37 mmol), with 20 ml of CH₂Cl₂ used for each component. The preparations followed generally the procedure described for the synthesis of compound 1, but the reactions were carried out at -78 °C. Yields, melting points and microanalyses: 2, 320 mg, 85%, m. p. 134 °C (decomp.); C₂₁H₁₅AuO₂PF₅ (619.27): calcd. C 40.5, H 2.4; found C 40.8, H 2.5. 3, 350 mg, 94 %, m.p. 138 °C (decomp.); C₂₄H₂₁AuO₂PF₅ (661.35) calcd. C 43.4, H 3.2, P 4.7; found C 43.1, H 3.3, P 4.6 %. 4, 240 mg, 97.5%, m.p. 132 °C (decomp.); C₂₃H₂₀AuO₂PF₅ (665.30): calcd. C 41.5, H 3.0, N 2.1; found C 40.9, H 2.8, N 1.9.

MS (FAB), 2: *m/z* 1081, 10% [(Ph₃PAu)₂OCOC₂F₅]⁺; 721, 18% [(Ph₃P)₂Au]⁺; 459, 100% [Ph₃PAu]⁺. 3: 1168, 6% {[(^pTol)₃PAu]₂OCOC₂F₅}⁺, 805, 56% {[(^pTol)₃P]₂-Au}⁺; 501, 100% [(^pTol)₃PAu]⁺. 4: 807, 53% {[(Me₂-NC₆H₄)Ph₂P]₂AuH}⁺; 304, 100% [(Me₂NC₆H₄)Ph₂P]⁺. NMR (CD₂Cl₂, 20 °C), 2, ¹H: 6.68 - 7.12, m, Ph. ¹³C{¹H}: 128.4, d, *J* = 67.7, C(*ipso*); 129.8, d, *J* = 12.3, C(*meta*); 132.7, d, *J* = 2.3, C(*para*); 134.6, d, *J* = 13.1, C(*ortho*). ¹⁹F{¹H}: -6.3, tr, ³J_{FF} = 112 Hz, CF₃; -42.7, q, ³J_{FF} = 112 Hz, CF₂. ³¹P{¹H}: 27.5, s, 3, ¹H: 2.4, s, 3H, Me; 7.1 - 7.7, m, 4H, C₆H₄. ¹³C{¹H}: 21.6, s, Me; 125.4, d, *J* = 70.0, C(*ipso*); 130.4, d, *J* = 12.3, C(*meta*); 134.4, d, *J* = 13.0, C(*ortho*); 143.5, d, *J* = 4.6, C(*para*). ³¹P{¹H}: 24.9, s, 4, ¹H: 3.0, s, 6H, Me; 6.74 and 7.36, d, 4H, C₆H₄; 7.38 - 7.42, m, 10H, Ph. ³¹P{¹H}: 24.8, s.

(^cHexylisocyanide)gold pentafluoropropionate (5)

As described for 2, C₂F₅COOAg (200 mg, 0.74 mmol) and (^cHexNC)AuCl (230 mg, 0.67 mmol) were reacted in a total of 25 ml of CH₂Cl₂ at -78 °C; yield 280 mg (89.2 %), m. p. 48 °C (decomp.). IR (KBr): 2253 cm⁻¹. MS (FAB): *m/z* 775, 100% [(^cHexNCAu)₂OCOC₂F₅]⁺; 470, 7.5% [MH]⁺. ¹H NMR (CD₂Cl₂, 20 °C): 1.52, 1.73, 1.97, and 3.80, m, C₆H₁₁ (2:4:4:1). C₁₀H₁₁NAuO₂F₅ (469.2) calcd. C 25.6, H 2.3, N 3.0; found C 25.0, H 2.2, N 2.8.

X-ray Crystallography. Specimens of suitable quality and size of compounds 1 and 3 were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on a Nonius DIP2020 diffractometer, employing graphite-monochromated Mo-K_α radiation. The structures were solved by a combination of direct methods (SHELXS-97) and difference-Fourier

syntheses and refined by full matrix least-squares calculations on F^2 (SHELXL-97). The atomic displacements are treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. Further information on crystal data, data collection and structure refinement are summarized in Table 1. Important interatomic distances and angles are given in the corresponding Figure Captions. Displacement parameters and complete tables of interatomic distances and angles have been deposited with the Cambridge Crystallo-

graphic Data Centre, CCDC-181633/4. Copies of the data can be obtained free of charge on application to the Director, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk)

Acknowledgements

This work was generously supported by Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Volkswagenstiftung, and Degussa AG.

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