

Gmelin Handbuch
der Anorganischen Chemie

Gmelin Handbuch der Anorganischen Chemie

Achte, völlig neu bearbeitete Auflage
8th Edition

Au Organogold Compounds

With 55 illustrations

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Bi	Bismut-Organische Verbindungen (Erg.-Werk, Bd. 47, 1977)
Co	Kobalt-Organische Verbindungen 1 (Erg.-Werk, Bd. 5, 1973) und 2 (Erg.-Werk, Bd. 6, 1973) sowie Kobalt Erg.-Bd. A (1961), B 1 (1963) und B 2 (1964)
Cr	Chrom-Organische Verbindungen (Erg.-Werk, Bd. 3, 1971)
Fe	Eisen-Organische Verbindungen A 1 (Erg.-Werk, Bd. 14, 1974), A 2 (Erg.-Werk, Bd. 49, 1977), A 3 (Erg.-Werk, Bd. 50, 1978), A 6 (Erg.-Werk, Bd. 41, 1977), B 1° (Erg.-Werk, Bd. 36, 1976), B 2* (1978), B 3° (1979), B 4 (1978), B 5 (1978), C 1 (1979), C 2 (1979), C 3* (1980) und Eisen B (1929–1932)
Hf	Organohafnium Compounds* (Erg.-Werk, Bd. 11, 1973)
Nb	Niob B 4 (1973)
Ni	Nickel-Organische Verbindungen 1 (Erg.-Werk, Bd. 16, 1975), 2 (Erg.-Werk, Bd. 17, 1974), Register (Erg.-Werk, Bd. 18, 1975) und Nickel B 3 (1966) und C (1968–1969)
Np, Pu	Transurane C° (Erg.-Werk, Bd. 4, 1972)
Pt	Platin C (1939) und D (1957)
Ru	Ruthenium Erg.-Bd. (1970)
Sn	Zinn-Organische Verbindungen 1 (Erg.-Werk, Bd. 26, 1975), 2 (Erg.-Werk, Bd. 29, 1975), 3 (Erg.-Werk, Bd. 30, 1976), 4 (Erg.-Werk, Bd. 35, 1976), 5 (1978) und 6 (1979)
Ta	Tantal B 2 (1971)
Ti	Titan-Organische Verbindungen 1 (Erg.-Werk, Bd. 40, 1977), 2 (1980)
V	Vanadium-Organische Verbindungen (Erg.-Werk, Bd. 2, 1971) und Vanadium B (1967)
Zr	Organozirkonium Compounds* (Erg.-Werk, Bd. 10, 1973)

* Completely or ° in part in English

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Preface

The present volume on organogold compounds covers the literature to the end of 1979.

While organogold chemistry was a research area only for a few individualists in the scientific community before 1955, it has enjoyed an ever increasing interest in the years since then. Apart from the general enthusiasm for organometallic chemistry typical of the 1960s and 1970s, this interest was generated by experimental evidence that organogold compounds may become important materials in the preparation of gold coatings for integrated circuits and for surface protection, in heterogeneous and homogeneous catalysis, and in pharmacology. Gold is still one of the most established and successful heavy metal drugs. It plays a significant role in space technology, and it is an essential element in modern electronics. It is therefore a pity, especially for further research, that the price of gold has increased so greatly over the last few years.

Nevertheless, it is the hope of the author that this volume will provide a sound basis for work in the future and that it will be a source of information for an increasing number of scientists with a love for gold chemistry in laboratories all over the world.

All compounds containing at least one gold-carbon bond have been included with the sole exception of gold cyanides and their complexes. The material has been arranged according to a Gmelin scheme which has now been used for several years for organometallic compounds. The compounds are classified first according to the number of Au atoms bonded to C atoms. For example, $(\text{CH}_3)_2\text{AuBr}_2\text{AuBr}_2$ is classed with the mononuclear complexes, while $[(\text{CH}_3)_2\text{AuCl}]_2$ is classed with the dinuclear compounds. Further division occurs according to the organic ligands. Here, the number of Au-C bonds which a ligand can form is determinative. Organic ligands are denoted with L, and ligands not connected by carbon, such as NH_3 or PR_3 , are denoted by D. In $^m\text{L}_n$ or $^u\text{D}_n$, the n indicates the number of ligands in the compound; the m, the number of Au-C bonds formed by the L ligand; and the u, the number of electrons which the D ligand provides for participation in the coordination bonds. Thus, CH_3 is a ^1L ligand, $\text{H}_2\text{C}=\text{CH}_2$ is a ^2L ligand, and norbornadiene may be considered as a ^4L ligand. $\text{P}(\text{CH}_3)_3$ is a ^2D ligand, and $(\text{CH}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CH}_3)_2$ is a ^4D ligand, although sometimes in bridged complexes it is denoted as $^2\text{D}-^2\text{D}$ for clarity. Further subdivisions are determined by the kind of ligand, e.g., alkyl or aryl, and the oxidation state of the Au atom.

It has not always been possible to indicate the compounds in a chapter exactly by general formulae in the heading. In these cases the user is referred to the introductory remarks, which characterize the substances more precisely.

Uncommon abbreviations have been avoided throughout, and international conventions followed for nomenclature, spectral data, and dimensions. The symbols η or h (eta or hapto) are not used. SI units are not enforced where the original article has Å, kcal, Debye, etc. The presentation of data in an abbreviated form, without the use of dimensions, is explained on p. 297.

The volume contains an empirical formula index on pages 298/317 and a ligand formula index on pages 318/49.

The author is grateful to Mrs. S. Schunke for typing the manuscript. May everyone feel that the work was worth undertaking.

Technische Universität München, Garching
Frankfurt/Main, Gmelin-Institut
March 1980

Hubert Schmidbaur
Adolf Slawisch

Table of Contents

	Page
1 Mononuclear Compounds	1
1.1 Compounds with Ligands Bonded by 1 C Atom	1
1.1.1 Compounds with One Alkyl Ligand (Type $^1\text{LAu}^2\text{D}$)	1
Gold (I) Compounds with One Unsubstituted Alkyl Ligand and Their Addition Compounds	2
Gold (I) Compounds with One Haloalkyl Ligand	22
Gold (I) Compounds with One Carbonyl Function in the Alkyl Group	24
Gold (I) 1,3-Diketones	26
Gold (I) Compounds Containing Ester and Cyano Functions in the Alkyl Ligand	27
Gold (I) Compounds Containing One Phosphonium Methylide Ligand	29
Gold (I) Compounds Containing One Silylmethyl Ligand	30
Gold (III) Compounds with One Alkyl Ligand	32
1.1.2 Compounds with Two Alkyl Ligands	36
Dialkylgold (I) Salts (Type $\text{M}[^1\text{LAu}^1\text{L}]$)	36
Gold (I) Compounds Containing One Alkyl and One Phosphonium Methylide Ligand	39
Bis(phosphonium-methylide)gold (I) Salts	40
Dialkyl-dihalo-, -dipseudohalo-, -dihydroxo-, or -oxalato-gold (III) Salts (Type $\text{M}[^1\text{L}_2\text{AuX}_2]$)	42
Dialkylgold (III) Tetrahaloaurates (III) of the Type $^1\text{L}_2\text{AuX}_2\text{AuX}_2$ or " $(^1\text{LAuX}_2)_2$ "	46
Dialkyl-monohalo-gold (III) Compounds (Type $^1\text{L}_2\text{Au}(^2\text{D})\text{X}$)	47
With Sulfur and Selenium Donors ^2D	48
With Nitrogen Donors ^2D	48
With Phosphorus, Arsenic, and Antimony Donors ^2D	50
Dialkyl-pseudohalogeno-gold (III) Compounds (Type $^1\text{L}_2\text{Au}(^2\text{D})\text{X}$)	54
With Nitrogen Donors ^2D	55
With Phosphorus and Arsenic Donors ^2D	56
With Sulfur Donors ^2D	57
Dialkylgold (III) Compounds of Type $^1\text{L}_2\text{Au}(^2\text{D})\text{X}$ with Various Other Groups X and ^2D	57
Dialkylgold (III) Compounds of the Type $[^1\text{L}_2\text{Au}(^2\text{D})_2]\text{X}$ and $[\text{cis-}^1\text{L}_2\text{Au}^4\text{D}]\text{X}$	60
With Two Oxygen or Sulfur Donors ^2D or One Sulfur Donor ^4D	61
With Two Nitrogen Donors ^2D or One Nitrogen Donor ^4D	62
With Two Phosphorus, Arsenic, or Antimony Donors ^2D or One Bidentate Donor ^4D , respectively	63
Dialkylgold (III) 1,3-Diketones	70
Dialkylgold (III) Dithiocarbamates, Selenothiocarbamates, and Xanthogenates (Dithiocarbonates)	73
Dialkylgold (III) Complexes with Mercapto Acids, Amino Acids, Iminophenols, and Aminomercaptanes	74
Gold (III) Compounds with Two Phosphonium Methylide Ligands (Type $[(\text{R}_3\text{PCH}_2)_2\text{AuX}_2]\text{Y}$)	77
1.1.3 Compounds with Three Alkyl Ligands	78
Gold (III) Compounds of the Type $^1\text{L}_3\text{Au}^2\text{D}$	80
With Three Methyl Ligands	80
With Two Methyl Ligands and One Other Alkyl Group	91

	Page
With Two or Three Ethyl Ligands	94
With Two Methyl Ligands and One Trifluoromethyl Ligand	95
With Methyl and 1,3-Diketone, Phosphonium Methylide, Alkenyl, Aryl, Isonitrile, and Alkynyl Ligands	95
1.1.4 Compounds with Four Alkyl Ligands	98
Tetraalkylgold(III) Salts of the Type $M[Au(^1L)_4]$	99
Gold(III) Compounds Containing Alkyl and Phosphonium or Sulfonium Methylide Ligands	101
1.1.5 Compounds with Alkenyl Ligands	104
Vinylgold(I) Complexes	104
Gold(I) Compounds with Fluoro, Cyano, and Ester Groups in the Alkenyl Ligand	106
Cyclopentadienylgold(I) Compounds	108
Ferrocenylgold(I) Compounds	109
With Unsubstituted Ferrocene	109
With Substituted Ferrocenes	113
Cymantrenylgold(I) Compounds	116
Alkenylgold(III) Compounds	117
1.1.6 Compounds with Two Alkenyl Ligands	117
Bis-ferrocenyl-gold(III) Compounds	117
1.1.7 Compounds with One Aryl Ligand	118
Arylgold(I) Complexes of Type $^1LAu^2D$	118
Phenyl- and Tolylgold(I) Complexes and Related Compounds	119
Halophenylgold(I) Complexes	121
Compounds of the Type $X_{5-n}H_nC_6Au^2D$ ($^2D = PR_3, AsR_3, SR_2$)	121
Compounds of the Type $X_{5-n}H_nC_6AuCNR$ ($X = F, Cl, Br$)	126
Carbene Compounds of the Type $C_6X_5AuC(R')NHR$ with $X = F, Cl, Br$, and $R' = OR'', NR''R'''$	128
Alkoxy- and Aminophenylgold(I) Complexes	128
Salts with Aryl(halo)gold(I) Anions, $M[^1LAuX]$	131
Arylgold(III) Dihalides, 1LAuX_2	131
Salts with Aryltrihalogold(III) Anions, Type $M[^1LAuX_3]$	132
Aryldihalogold(III) Complexes of the Type $^1LAu(^2D)X_2$, $^1LAu(CNR)X_2$, and $^1LAu(CRR')X_2$	134
Compounds of the Type $^1LAu(^2D)X_2$ with $^2D = OR_2, SR_2$	134
Compounds of the Type $^1LAu(^2D)X_2$ with Group V Donors 2D	136
Compounds of the Type $C_6F_5Au(CNR)X_2$	140
Carbene Compounds of the Type $C_6F_5Au(CRR')X_2$	140
1.1.8 Compounds with Two Aryl Ligands	141
Diarylgold(I) Salts (Type $M[Au(^1L)_2]$)	141
Diaryl-dihalo-gold(III) Salts (Type $M[^1L_2AuX_2]$)	142
Diarylgold(III) Compounds of the Type $^1L_2Au(^2D)X$	143
The Compound $(C_6Cl_5)_2Au(P(C_6H_5)_3)Cl$	143
Compounds of the Type $cis-(C_6F_5)_2Au(P(C_6H_5)_3)X$	143
Compounds of the Type $cis-(C_6F_5)_2Au(As(C_6H_5)_3)X$	147
The Compound $(C_6F_5)_2Au(CNC_6H_5)Cl$	147
Diarylgold(III) Compounds of the Type $[(C_6F_5)_2Au(P(C_6H_5)_3)^2D]X$	149
1.1.9 Compounds with Three Aryl Ligands	150
1.1.10 Compounds with Four Aryl Ligands	151

	Page
1.1.11. Compounds with Carbonyl Ligands	152
Matrix Isolated Binary Carbonyls of Gold(0) and Their Oxidation Products	152
Carbonyl(halo)gold(I) Complexes	158
1.1.12 Compounds with One Isonitrile Ligand	161
Gold(I) Compounds with One Isonitrile Ligand	162
Compounds of the Type RNCAuX	162
Compounds of the Type RNCAu^1L	165
Compounds of the Type $[\text{cyclo-C}_6\text{H}_{11}\text{NCAuC(R)R}']\text{ClO}_4$	165
Gold(III) Compounds with One Isonitrile Ligand (Type RNCAuCl_3)	166
1.1.13 Gold(I) Compounds with Two Isonitrile Ligands (Type $[(\text{RNC})_2\text{Au}]\text{X}$)	167
1.1.14 Gold(I) Compounds with Four Isonitrile Ligands (Type $[(\text{RNC})_4\text{Au}]\text{X}$)	169
1.1.15 Compounds with Carbeniate or Carbene Ligands	169
[Alkoxy(imino)carbeniate](triphenylphosphine)gold(I) Compounds (Type $(\text{C}_6\text{H}_5)_3\text{PAuC(=NR')OR}$)	170
[Alkoxy(amino)carbene](triphenylphosphine)gold(I) Salts (Type $[(\text{C}_6\text{H}_5)_3\text{PAuC(NHR')OR}]\text{X}$)	172
[Alkoxy(amino)carbene]gold(I) Halides (Type XAuC(NHR')OR)	173
[Bis(amino)carbene](triphenylphosphine)gold(I) Salts (Type $[(\text{C}_6\text{H}_5)_3\text{PAuC(NHR')}_2]\text{X}$)	175
[Bis(amino)carbene]gold(I) Chlorides (Type ClAuC(NHR')NHR)	176
Alkoxy(amino)carbenegold(III) Compounds (Type $\text{Cl}_3\text{AuC(NHR')OR}$)	178
1.1.16 Compounds with Two Carbeniate or Carbene Ligands	178
Bis[alkoxy(amino)carbene]gold(I) Salts (Type $[(\text{RO(R'NH)C})_2\text{Au}]\text{X}$)	178
Bis[amino(imino)carbeniate]gold Salts (Type $\text{M[AuC(=NR)NR'R'']}_2$)	179
Bis[bis(amino)carbene]gold(I) Salts (Type $[(\text{RNH(R'R''N)C})_2\text{Au}]\text{X}$)	180
Bis(carbene)dihalogold(III) Salts (Type $[(\text{R(R')C})_2\text{AuX}_2]\text{X'}$)	187
1.1.17 Compounds with Four Carbeniate Ligands (Type $[\text{As}(\text{C}_6\text{H}_5)_4][\text{Au}^1\text{L}_4]$ with $^1\text{L}=\text{Tetrazolyl Derivatives}$)	189
1.1.18 Compounds with Alkynyl Ligands	191
Compounds Containing One Alkynyl Ligand (Type $\text{RC}=\text{CAu}^2\text{D}$)	191
Compounds Containing Two Alkynyl Ligands (Type $\text{K[Au(C}\equiv\text{CR)}_2]$)	194
1.2 Compounds with Ligands Bonded by 2 C Atoms	194
1.2.1 Gold Complexes of Alkenes	195
(Alkene)gold(0) Compounds	195
Gold(I) Complexes with One Monoolefin Bonded to Gold, Type $^2\text{LAuX}$	197
Complexes of the Type $^2\text{LAuCl}$ with $^2\text{L}=\text{Open-Chain Monoolefin}$	198
Complexes of the Type $^2\text{LAuCl}$ with $^2\text{L}=\text{Cyclic Monoolefin}$	201
Compounds of the Type $^2\text{LAuOSO}_2\text{X}$ with $\text{X}=\text{F, CF}_3$	201
Gold(I) Complexes with One Polyolefin Bonded to Gold Through Two C Atoms, Type $^2\text{LAuX}$ and $[\text{LAu}^2\text{D}]\text{X}$	203
Gold(I) Complexes with Two Monoolefins Bonded to Gold Through Two Carbon Atoms, Type $[\text{L}_2\text{Au}]\text{AuCl}_4$	205
Gold(I) Complexes with Two Diolefins Bonded to Gold Through Two Carbon Atoms, Type $[\text{L}_2\text{Au}]\text{X}$	206

	Page
Gold (I) Complexes with Three Olefins Bonded to Gold Through Two Carbon Atoms, Type 2L_3AuX	206
Interaction of Alkenes with Gold Metal	208
Interaction of Alkenes with Gold (III) Salts	208
1.2.2 Gold Complexes of Alkynes (Acetylenes)	209
(Alkyne)gold (0) Compounds	209
Gold (I) Complexes with One Alkyne Bonded to Gold, Type 2LAuX	209
Gold (III) Complexes with One Alkyne Bonded to Gold	210
Complexes with Two Alkynes Bonded to Gold	211
1.2.3 Gold Complexes of Carbaboranes	212
Gold Complexes Containing One Carbaborane Ligand	212
Gold Complexes Containing Two Carbaborane Ligands	215
1.2.4 Gold-containing Metallocyclic Compounds	217
Cyclomethylenegold (III) Complexes	217
Aura-cyclopentadiene Complexes	218
1.3 Compounds with Ligands Bonded by 4 C Atoms	219
1.3.1 Gold (I) Compounds of Di- and Tetraolefins, Type 4LAuX	219
1.3.2 Gold (III) Compounds of Diolefins	220
2 Binuclear Compounds	222
2.1 Compounds with Ligands Bonded by 1 C Atom	222
2.1.1 Compounds with Two Alkyl Ligands	222
2.1.2 Compounds with Four Alkyl Ligands	222
The Dimeric Dialkylgold (III) Halides (1L_2AuX) ₂	222
The Dimeric Dialkylgold (III) Pseudohalides, Hydroxide, Siloxide, Sulfates, and Phosphates (1L_2AuX) ₂ and [1L_4Au_2X_2] ²⁻	229
The Dinuclear Dialkylgold (III) Halides or Pseudohalides with Difunctional Donors, X(1L) ₂ Au ^{2D-2} DAu(1L) ₂ X	232
The Dimeric Dialkylgold (III) Carboxylates and Thiocarboxylates	235
The Dimeric Dialkylgold (III) Salicylaldimides, Thiolates, Selenolates, and Phosphides	237
2.1.3 Compounds with Six Alkyl Ligands	238
2.1.4 Compounds with One Alkenyl Group	238
Salts of 1,1-Bis-triorganophosphinegold (I)-Substituted Olefins	238
Salts of 1,1-Bis-triarylphosphinegold (I)-Substituted Ferrocenes and Cymantrenes	240
2.1.5 Compounds with One Aryl Group	246
Aryl-1,1-bis (triorganophosphinegold (I)) Salts	246
2.1.6 Compounds with Two Aryl Groups	249
Arylgold (I) Complexes of Difunctional Ligands	249
The Dimeric Arylgold (III) Dihalides	250
Dihalo(phenyl)gold (III) Complexes of Difunctional Ligands	252
Other Diaryldigold Compounds	254

	Page
2.1.7 Compounds with Four Aryl Groups	255
Diaryl(halo)gold(III) Complexes of Difunctional Ligands	255
Bis-diaryl(triphenylphosphine)gold(III) Pseudohalide or Sulfate Complexes	256
2.1.8 Dinuclear Alkyne Compounds	256
2.2 Compounds with Ligands Bonded by 2 C Atoms	256
2.2.1 Compounds with One Dialkylphosphonium-bis-methylide Ligand	256
2.2.2 Compounds with Two α , ω -di- σ -bonded Alkyl Groups	257
2.2.3 Compounds with Two Dialkylphosphonium-bis-methylide Ligands	257
The Dimeric Gold(I) Dialkylphosphonium-bis-methylides, $R_2P(CH_2AuCH_2)_2PR_2$	257
The Dimeric Halogeno-gold(II) Dialkylphosphonium-bis-methylides, $R_2P(CH_2Au(X)CH_2)_2PR_2$	260
The Dimeric Dihalogeno-gold(III) Dialkylphosphonium-bis-methylides, $R_2P(CH_2Au(X_2)CH_2)_2PR_2$	263
Mixed Alkyl/Dialkylphosphonium-bis-methylide Species	263
2.2.4 Compounds with One Alkenyl Ligand	264
2,3-Bis-triorganophosphinegold(I)-but-2-enes	264
2-Triorganophosphinegold(I)-3-triorganophosphinedialkylgold(III)-but-2-enes	266
2.2.5 Compounds with Two α , ω -di- σ -bonded Buta-1,3-diene Ligands	268
2.2.6 1,6-Bis(triphenylgold)ferrocene	269
2.2.7 Aryl-Bridged Polymetallic Gold Compounds	269
2.3 Compounds with Ligands Bonded by 4 C Atoms	273
2.3.1 Compounds of the Type $^4L(AuCl)_2$ (4L = Alkadiene)	273
3 Trinuclear Compounds	275
3.1 Trinuclear Dialkylgold(III) Compounds	275
3.1.1 Tris-dialkylgold(III) Phosphates	275
3.1.2 Trimeric Di-n-butylgold Ferrocenethiolate	275
3.2 Trimeric 2-Pyridylgold(I) Compounds	275
3.3 Trimeric Gold(I) Carbeniate Complexes	276
3.4 Trinuclear Halogenogold(I/III) and Halogenogold(III) Carbeniate Complexes	280
4 Tetranuclear Compounds	282
4.1 Dialkylgold(III) Hydroxides, Sulfates, Phenylphosphate, and Phenylarsonate	282
4.2 Dialkylgold(III) Dicarboxylates	284
4.3 Dialkylgold(III) Cyanides	286
4.4 Gold(I) Acetylides	290
5 Hexanuclear Compounds	291

	Page
6 Polynuclear Compounds	292
6.1 Dialkylgold(III) Carboxylates, Imidazolates, and Triazolates	292
6.2 Dialkylgold(III) Gold(I) Dicyanides	293
6.3 Gold(I) Ketenide, N-Methyl-benzimidazolate, Pyrrolide, Diphosphinomethanide, and a Polymeric Phosphonium Ylide Complex	293
6.4 Gold(I) Aryls	295
6.5 Gold(I) Acetylides	296
Abbreviations and Dimensions	297
Empirical Formula Index	298/317
Ligand Formula Index	318/49
Table of Conversion Factors	350/1

Gold-Organic Compounds

The general literature is given in the individual chapters. For abbreviations used throughout this volume see p. 297 and preface.

1 Mononuclear Compounds

1.1 Compounds with Ligands Bonded by 1 C Atom

1.1.1 Compounds with One Alkyl Ligand (Type $^1\text{LAu}^2\text{D}$)

General Literature:

- R. J. Puddephatt, *The Chemistry of Gold*, Elsevier, Amsterdam 1978, p. 100/2.
- R. J. Puddephatt, *Reactivity and Mechanism in Organogold Chemistry*, *Gold Bull.* **10** [1977] 108/13.
- H. Schmidbaur, *Ist Gold-Chemie aktuell?*, *Angew. Chem.* **88** [1976] 830/43; *Is Gold Chemistry a Topical Field of Study?*, *Angew. Chem. Intern. Ed. Engl.* **15** [1976] 728/40.
- B. F. G. Johnson, *Recent Advances in Organogold Chemistry*, *Gold Bull.* **9** [1976] 46/9.
- J. K. Kochi, *Electron-Transfer Mechanism for Organometallic Intermediates in Catalytic Reactions*, *Accounts Chem. Res.* **7** [1974] 351/60.
- B. Armer, H. Schmidbaur, *Organogold-Chemie*, *Angew. Chem.* **82** [1970] 120/33; *Organogold Chemistry*, *Angew. Chem. Intern. Ed. Engl.* **9** [1970] 101/14; *Usp. Khim.* **40** [1971] 1211/22.
- E. Müller, Houben-Weyl, *Methoden der Organischen Chemie*, 4th Ed., Vol. 13, Pt. 1, G. Thieme, Stuttgart 1970, p. 783/99.
- Gmelin Handbuch "Gold" **3**, 1954, p. 726/7.

General Comments

Simple alkylgold compounds of the formula ^1LAu are unknown. All attempts to synthesize species of this type have failed, but numerous complexes with a variety of donor molecules, especially phosphines, could be prepared, and their composition, structure, bonding, and reactivity are well established. They invariably belong to the class $^1\text{LAu}^2\text{D}$ with only one ^2D ligand attached to the gold center. In no case has been observed a coordination number greater than two for gold(I) compounds bearing an alkyl ^1L ligand attached to the metal. $^1\text{LAu}(^2\text{D})_2$ species were discussed as intermediates or transition states of substitution reactions (see p. 12), but there is no conclusive evidence for such three-coordinate complexes.

In agreement with theoretical predictions, $^1\text{LAu}^2\text{D}$ molecules have a linear structure, which has been confirmed in at least one X-ray diffraction study [3]. Spectroscopic data are also in agreement with a linear arrangement [2].

The synthesis of $^1\text{LAu}^2\text{D}$ compounds was first achieved by alkylation of $\text{Au}(^2\text{D})\text{X}$ precursors ($\text{X} = \text{halogen}$) with alkyllithium reagents [1]. This procedure is still the method of choice for most of the complexes prepared to date. Other routes, like the Grignard reaction or the thermal decomposition of Au^{III} compounds, can only be applied in special cases. For a particular alkyl ^1L ligand a series of complexes can be obtained through substitution of the ^2D donor ligand.

The compounds with phosphine donors ($^2\text{D} = \text{PR}_3$) are colorless, low-melting solids or liquids, which are metastable and decompose on heating. When stored at room temperature, they decompose slowly with the formation of metallic gold. This decomposition is enhanced by light in some cases; thus, the compounds should be kept in the dark. They are not sensitive to air and moisture and appear to be oxidized or hydrolyzed only very slowly. The complexes are soluble in many organic solvents, both polar and non-polar. They dissolve as monomers, as proven by molecular mass determinations. Some of them are volatile in a vacuum and monomers are observed in the vapor phase by mass spectrometry.

$^1\text{LAu}^2\text{D}$ compounds with ^2D donors other than phosphines are much less stable and only a few complexes of this type have been reported.

Literature:

[1] G. Calvin, G. E. Coates, P. S. Dixon (Chem. Ind. [London] 1959 1628). — [2] C. F. Shaw, R. S. Tobias (Inorg. Chem. 12 [1973] 965/78). — [3] P. D. Gavens, J. J. Guy, M. J. Mays, G. Sheldrick (Acta Cryst. B 33 [1977] 137/9).

1.1.1.1 Gold(I) Compounds with One Unsubstituted Alkyl Ligand and Their Addition Compounds

$\text{CH}_3\text{AuP}(\text{CH}_3)_3$. The principal method of preparation for this compound is the methylation of $\text{Au}(\text{P}(\text{CH}_3)_3)\text{X}$ complexes ($\text{X} = \text{halogen}$) using methylolithium. This reaction has to be carried out at low temperature in order to avoid decomposition [2]. Cooling to -10°C seems to be sufficient, as yields of 91% were recorded for this temperature. Diethylether is the preferred solvent. A slight excess of the CH_3Li reagent is of advantage (molar ratio 1:1.2) [7]. In a standard procedure the two components are allowed to react in ether at -10°C for 30 min, the mixture is agitated for another 2 h at 20°C and then hydrolyzed with ice-cold water. The ether extract after drying yields the product upon evaporation of the solvent [4, 7, 35].

Physical Properties

The compound forms soft, colorless crystals of melting point 70 to 71°C [7, 32], 75 to 75.5°C [3]. It can be sublimed at $53^\circ\text{C}/0.1$ Torr [7]. Its dipole moment has been determined in benzene solvent under conditions not specified any further: $\mu = 5.4$ to 5.6 D [3].

^1H NMR data are available for various solvents and the results give important information on the ligand exchange properties of this compound. In benzene in the absence of excess phosphine ligand and other impurities, two ^1H signals are observed: $\delta = 0.15$ (d, CH_3P , 9H, $^2\text{J}(\text{PH}) = 8.9$), 0.55 (d, CH_3Au , 3H, $^3\text{J}(\text{PH}) = 8.7$) [32]. Under the same conditions $^1\text{J}(\text{CH}) = 129$ and $^1\text{J}(\text{CH}) = 124$, respectively, have been determined for these signals from satellite lines [7]. Upon addition of traces of trimethylphosphine to the solution, the coupling $^3\text{J}(\text{PH})$ in the CH_3Au signal disappears due to rapid exchange of the phosphine ligands at the gold center. The coupling $^2\text{J}(\text{PH})$ of the CH_3P becomes a function of the relative molar concentrations C_A , C_B of the complex and the free ligand: $\bar{J} = C_A \cdot J_A + C_B \cdot J_B$. At a molar ratio of the two components of 1:3.4, the observed $\bar{J}$ value therefore becomes zero for the system under rapid exchange [33]. From this concentration dependence it can be proven, that $^2\text{J}(\text{PH})$ is of opposite sign in the complex and in the free ligand: $^2\text{J}(\text{PH})_{\text{complex}} = -8.9$, $^2\text{J}(\text{PH})_{\text{ligand}} = +2.6$ [7]. From the concentration dependence of the coalescence temperature for the CH_3Au signal, a free energy of activation $\Delta G^\ddagger = 7$ kcal/mol and a frequency factor $A = 10^7$ have been derived [33].

Literature see p. 21/2

^1H NMR data for other solvents are as follows (compare p. 297):

Solvent	$\delta(\text{CH}_3\text{Au})$	$^3\text{J}(\text{PH})$	$\delta(\text{CH}_3\text{P})$	$^2\text{J}(\text{PH})$	Lit.
Acetone- d_6	0.07	8.4	1.36	9.0	[38]
CH_3I	0.90	8.4	2.30	9.0	[38]
CH_3I	1.12	8.5	2.52	8.9	[16]
CH_2Cl_2	0.58	8.0	1.75	9.0	[22]
Benzene	0.57	8.7	0.28	8.9	[7]
CDCl_3	0.09	8.6	1.38	8.6	[36]

The ^{197}Au Mössbauer spectrum (at 4 K, Au/Pt reference) shows a doublet signal with an isomeric shift $\delta = 4.90 \pm 0.10$ and a quadrupole splitting $\Delta = 10.21 \pm 0.20 \text{ mm} \cdot \text{s}^{-1}$ [46].

The IR spectrum was initially recorded for the region 200 to 3500 cm^{-1} and bands at 357, 1159, and 1170 cm^{-1} have been assigned to the $\nu(\text{AuP})$ and $\delta(\text{CH}_3\text{Au})$ vibrations, respectively (in Csl) [3]. Nujol solutions showed $\nu(\text{AuP})$ at 356 and $\delta(\text{CH}_3\text{Au})$ at 1159 cm^{-1} . Further assignments included: 531 $\nu(\text{AuC})$, 696 $\rho(\text{CH}_3\text{Au})$, 680, 742 $\nu(\text{PC}_3)$, 844, 852, 940, 960 $\rho(\text{CH}_3\text{P})$, 1294, 1300, 1302, 1419, 1430 $\delta(\text{CH}_3\text{P})$ [7].

In the Raman spectrum the corresponding $\nu(\text{AuP})$ line appears at 360, $\nu(\text{AuC})$ at 536. Other lines are reported at 230, 247, 317, and 410 [7]. A virtually complete and very detailed IR and Raman analysis of the compound confirmed most of the earlier assignments. The new data were summarized as in Table 1 [36].

Table 1

Vibrational spectra (cm^{-1}) of $\text{CH}_3\text{AuP}(\text{CH}_3)_3$ and $\text{CD}_3\text{AuP}(\text{CH}_3)_3^{\text{a)}$.

^{a)} Key: s = strong, m = medium, w = weak, b = broad, p = polarized, sh = shoulder. ^{b)} 632.8 nm excitation. ^{c)} 488.0 and 501.7 nm excitation.

Qualitative assignment	$\text{CH}_3\text{AuP}(\text{CH}_3)_3$			$\text{CD}_3\text{AuP}(\text{CH}_3)_3$		
	Raman Powder ^{b)}	Benzene solution ^{c)}	Mull	Infrared CDCl_3 , CS_2 solution	Mull	Infrared CDCl_3 , CS_2 solution
$\delta(\text{CAuP})$	115 w	—	—	—	—	—
$\rho(\text{C}_3\text{PAu})$	188 sh	—	—	—	—	—
$\nu(\text{AuP}) + \delta_s(\text{C}_3\text{P})$	200 m 210 sh	200 m, p	—	—	—	—
$\delta_{\text{as}}(\text{C}_3\text{P})$	217 m	266 s, dp	—	—	265 w	268 w
$\delta_s(\text{C}_3\text{P}) + \nu(\text{AuP})$	359 w	353 w, p	356 w	—	359 w	356 m
$\nu(\text{AuCD}_3)$	—	—	—	—	479 m 485 m	489 s
$\rho(\text{CD}_3\text{Au})$	—	—	—	—	537 m, b	543 m, b
$\nu(\text{AuCH}_3)$	531 s 536 s	539 s, p	528 m 534 m	539 m	—	—
$\nu_s(\text{C}_3\text{P})$	681 m	678 w, p	681 w 696 w	678 m	681 m	679 w
$\rho(\text{CH}_3\text{Au})$	—	710 w	—	710 m, b	—	—

Literature see p. 21/2

1*