Gmelin Handbuch

der Anorganischen Chemie

Gmelin Handbuch der Anorganischen Chemie

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Au
Organogold Compounds

With 55 illustrations

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The following listing indicates in which volumes these compounds are discussed or are referred to:

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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)
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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	Organozirconium Compounds* (Erg.-Werk, Bd. 10, 1973)

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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, $(CH_3)_2AuBr_2AuBr_2$ is classed with the mononuclear complexes, while $[(CH_3)_2AuCl]_2$ 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 ${}^{m}L_n$ or ${}^{u}D_n$, 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 ${}^{1}L$ ligand, $H_2C{=}CH_2$ is a ${}^{2}L$ ligand, and norbornadiene may be considered as a ${}^{4}L$ ligand. $P(CH_3)_3$ is a ${}^{2}D$ ligand, and $(CH_3)_2PCH_2CH_2P(CH_3)_2$ is a ${}^{4}D$ ligand, although sometimes in bridged complexes it is denoted as ${}^{2}D$-${}^{2}D$ 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 — Hubert Schmidbaur

Frankfurt/Main, Gmelin-Institut — Adolf Slawisch

March 1980

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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 $^1LAu^2D$)

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 $^1LAu^2D$ 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. $^1LAu(^2D)_2$ 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, $^1LAu^2D$ 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 $^1LAu^2D$ compounds was first achieved by alkylation of $Au(^2D)X$ precursors (X = 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 ($^2D = PR_3$) 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.

$^1LAu^2D$ 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

$CH_3AuP(CH_3)_3$. The principal method of preparation for this compound is the methylation of $Au(P(CH_3)_3)X$ complexes (X = halogen) using methyllithium. 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°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, 9 H, $^2J(PH) = 8.9$), 0.55 (d, CH_3Au, 3 H, $^3J(PH) = 8.7$) [32]. Under the same conditions $^1J(CH) = 129$ and $^1J(CH) = 124$, respectively, have been determined for these signals from satellite lines [7]. Upon addition of traces of trimethylphosphine to the solution, the coupling $^3J(PH)$ in the CH_3Au signal disappears due to rapid exchange of the phosphine ligands at the gold center. The coupling $^2J(PH)$ 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 J value therefore becomes zero for the system under rapid exchange [33]. From this concentration dependence it can be proven, that $^2J(PH)$ is of opposite sign in the complex and in the free ligand: $^2J(PH)_{complex} = -8.9$, $^2J(PH)_{ligand} = +2.6$ [7]. From the concentration dependence of the coalescence temperature for the CH_3Au signal, a free energy of activation $\Delta G^{\neq} = 7$ kcal/mol and a frequency factor $A = 10^7$ have been derived [33].

Literature see p. 21/2

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

Solvent	$\delta(CH_3Au)$	$^3J(PH)$	$\delta(CH_3P)$	$^2J(PH)$	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 $\Delta = 10.21 \pm 0.20$ mm · 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 ν(AuP) and $\delta(CH_3Au)$ vibrations, respectively (in CsI) [3]. Nujol solutions showed ν(AuP) at 356 and $\delta(CH_3Au)$ at 1159 cm^{-1}. Further assignments included: 531 ν(AuC), 696 $\rho(CH_3Au)$, 680, 742 $\nu(PC_3)$, 844, 852, 940, 960 $\rho(CH_3P)$, 1294, 1300, 1302, 1419, 1430 $\delta(CH_3P)$ [7].

In the Raman spectrum the corresponding ν(AuP) line appears at 360, ν(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 $CH_3AuP(CH_3)_3$ and $CD_3AuP(CH_3)_3$[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	$CH_3AuP(CH_3)_3$				$CD_3AuP(CH_3)_3$	
	Raman		Infrared		Infrared	
	Powder[b]	Benzene solution[c]	Mull	$CDCl_3$, CS_2 solution	Mull	$CDCl_3$, CS_2 solution
δ(CAuP)	115 w	—	—	—	—	—
$\rho(C_3PAu)$	188 sh	—	—	—	—	—
$\nu(AuP) + \delta_s(C_3P)$	200 m 210 sh	200 m, p	—	—	—	—
$\delta_{as}(C_3P)$	217 m	266 s, dp	—	—	265 w	268 w
$\delta_s(C_3P) + \nu$(AuP)	359 w	353 w, p	356 w	—	359 w	356 m
$\nu(AuCD_3)$	—	—	—	—	479 m 485 m	489 s
$\rho(CD_3Au)$	—	—	—	—	537 m, b	543 m, b
$\nu(AuCH_3)$	531 s 536 s	539 s, p	528 m 534 m	539 m	—	—
$\nu_s(C_3P)$	681 m	678 w, p	681 w 696 w	678 m	681 m	679 w
$\rho(CH_3Au)$	—	710 w	—	710 m, b	—	—

Literature see p. 21/2

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