Coordination of the Hetero(N,S)-bidentate Ligand 1-Methyl-2-(methylthiomethyl)-1*H*-benzimidazole to $[(Ph_3P)Au]^+$ Exclusively through the Imine Nitrogen Donor

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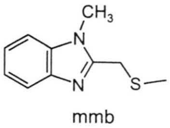
Z. Naturforsch. **54b**, 1606–1608 (1999); received September 17, 1999

Gold(I) Complex, Benzimidazole Ligand, Thioether

1-Methyl-2-(methylthiomethyl)-1*H*-benzimidazole (mmb, N^S) was reacted with $Ph_3PAuCl/AgPF_6$ in THF to yield $[(Ph_3P)Au(mmb)](PF_6)$ which could be crystallographically characterized. The Au^+ ion is almost linearly coordinated by the triphenylphosphine P and the imine N atom of a monodentate N^S ligand. There is no gold(I)-sulfur bonding as the distance of *ca.* 3.02 Å indicates. Similarly, close intermetallic contacts between the gold centers are absent. Both effects are attributed to the positive charge on the metal.

The affinity between gold in low oxidation states and sulfur centers of corresponding ligands is well established and of considerable practical value. This includes the stability of gold thiolate drugs for treating rheumatoid arthritis [1,2], the formation of self-assembled thiol monolayers on gold surfaces [3] and the process of gilding by using Au/S-based preparations [1,4]. Among the possible sulfur-containing ligands for Au^I are thioethers which have been studied e.g. in the form of complexes $[XAu(SR_2)]^{n+}$, X = Hal and n = 0 [4] or X = PPh_3 and n = 1 [1].

Herein we report the result of the reaction between the $Ph_3PAuCl/AgPF_6$ system and the N,S-chelate ligand 1-methyl-2-(methylthiomethyl)-1*H*-benzimidazole (mmb) [5].



mmb

The N^S ligands were structurally shown to bind as chelates to Rh^{III}, Ir^{III}, Cu^I, Cu^{II} and Ag^I centers [6–9]. As ligand to quinone-copper units the N^S molecules permit the observation of an unusual reversible valence tautomer equilibrium (1) [5,7].

$$(N^\wedge S)Cu^{I}(Q^{\cdot -}) \rightleftharpoons (N^\wedge S)Cu^{II}(Q^{2-}) \qquad (1)$$

Q = *o*-quinone

The stability of the P-Au bond in the $[(Ph_3P)Au]^+$ fragment raised the question whether the N^S ligand would bind in bi- or monodentate fashion and, if the latter were true, which of the donor centers would be coordinated, the softer thioether sulfur or one of the more basic nitrogen atoms.

Results and Discussion

Addition of 1-methyl-2-(methylthiomethyl)-1*H*-benzimidazole to the freshly prepared $[(Ph_3P)Au](PF_6)$ system in THF yielded colorless $[(Ph_3P)Au(mmb)](PF_6)$ in good yield. Elemental analysis, NMR characterization (^1H, ^{13}C, ^{31}P; see Exp. Section) and especially the X-ray diffraction study (Table I) established the identity of the compound.

The result of the structure determination is illustrated in Fig. 1, showing one of the two crystallographically independent cations.

The gold(I) cation in $[(Ph_3P)Au(mmb)](PF_6)$ is coordinated almost linearly (*ca.* 175°) by the triphenylphosphine P atom and by the imine center of the N^S ligand. At 3.028(3)/3.017(2) Å the Au--S distance is close to the sum of the van der Waals radii and certainly much longer than the 2.3228(12) Å found for $[(Ph_3P)Au(Me_2S)](O_3SCF_3)$ [1]. Compounds of Ag^I or Cu^I with N^S ligands have metal sulfur distances of about 2.70 Å (Ag^I) and 2.43–2.62 Å (Cu^I) [6,9]. The bond parameters in Fig. 1 clearly illustrate that the gold center in $[(Ph_3P)Au(mmb)](PF_6)$ is two-coordinate and the N^S ligand effectively monodentate. Interestingly, it is not the soft thioether sulfur atom but the more basic imine nitrogen site of N^S which is preferred by the gold(I) center. As has been noted before [4], the $[(PPh_3)Au]^+$ ion has a "hard" electrophilic character, similar to H^+, which would explain its preference for neutral N over neutral S donors.

0932–0776/99/1200–1606 $06.00

Table I. Crystallographic data for $[(Ph_3P)Au(mmb)](PF_6)$.

Empirical formula	$C_{28}H_{27}AuF_6N_2P_2S$
Formula weight	796.48
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	P2(1)/n
a (Å)	10.7529(7)
b (Å)	19.4625(10)
c (Å)	28.431(2)
β (°)	90.549(8)
V (Å^3)	5949.8(7)
Z	4
Calc. density (Mg/m^{-3})	1.778
Absorption coefficient, μ (mm^{-1})	5.182
F(000)	3104
θ-Range (°)	2.02 to 25.95
Limiting indices	$-12 \leq h \leq 13$, $-23 \leq k \leq 23$, $-34 \leq l \leq 34$
Reflections collected	46298
Independent reflections	11555
R_{int}	0.1192
Data / Restraints / Parameters	11555 / 0 / 721
Goodness-of-fit on F^2 [a]	0.555
Final R indices [I>2σ(I)]	$R1 = 0.0353$, $wR2 = 0.0465$
R Indices (all data) [b,c]	$R1 = 0.1370$, $wR2 = 0.0635$
Largest diff. peak and hole (e Å^{-3})	0.501 and −1.323

[a] GOF = $\{\Sigma w(|F_o|^2 - F_c|^2)^2/(n\text{-}m)\}^{1/2}$; n = number of data; m = number of variables.

[b] $R = (\Sigma \| F_o| - |F_c\|)/\Sigma |F_o|$.

[c] $R_w = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2]/\Sigma[w(F_o4)]\}^{1/2}$.

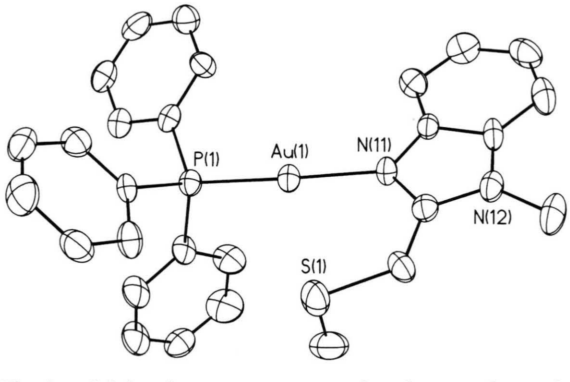


Fig. 1. Molecular structure of the cation in $[(Ph_3P)Au(mmb)](PF_6)$ with atomic numbering. (ORTEP, 50% probability ellipsoids; hydrogen atoms are obmitted for clarity; only one of the two crystallographically independent species is shown). Selected distances [Å] and angles [°]: Au(1)–N(11) 2.080(6), Au(2)–N(21) 2.076(6); Au(1)–P(1) 2.235(2), Au(2)–P(2) 2.234(2); Au(1)–S(1) 3.028(3), Au(2)–S(2) 3.017(2); N(11)–Au(1)–P(1) 175.49(19), N(21)–Au(2)–P(2) 174.1(2); S(1)–Au(1)–P(1) 109.53(08), S(2)–Au(2)–P(2) 110.24(07); N(11)–Au(1)–S(1) 74.3(2), N(21)–Au(2)–S(2) 74.1(2).

A structure related to that of the cation $[(Ph_3P)Au(mmb)]^+$ has been described earlier for neutral $(Ph_3P)Au$(dedtc), where dedtc is monodentate diethyldithiocarbamate with a bonding (2.338(3) Å) and non-bonding Au-S distance (3.015(3) Å) [10]. Even 2,2′-bipyridine with two equivalent chelate donor centers binds in unsymmetrical fashion to the $[(Ph_3P)Au]^+$ fragment with Au-N distances of 2.166(2) and 2.406(2) Å and an obtuse angle P–Au–N of 157.1(1)° [11]. Related "2+1" coordination has similarly been observed for Hg^{II} and Cu^{I} species [12].

There are no significant intermolecular interactions in the crystal of $[(Ph_3P)Au(mmb)](PF_6)$, specifically, the metal-metal distances of >6.5 Å are outside of any bonding range. We attribute this result to the positive charge at the gold(I) centers, the Au^+-Au^+ electrostatic repulsion and steric effects override the relativistic effects deemed responsible for aurophilic attractions [13].

Experimental Section

All experiments were carried out under an atmosphere of dry argon. Standard equipment was used throughout.

(1-Methyl-2-(methylthiomethyl)-1H-benzimidazole)(triphenylphosphine)gold(I) hexafluorophosphate

A solution of 50 mg (0.1 mmol) of Ph_3PAuCl in 15 ml of THF was treated at 0 °C with a solution of 26 mg (0.1 mmol) of $AgPF_6$ in 3 ml of THF. After 10 min stirrring and filtration, 20 mg (0.1 mmol) of 1-methyl-2-(methylthiomethyl)-1*H*-benzimidazole [5] was added in 5 ml of THF and the mixture warmed to room temperature. After 30 min stirring, volume reduction to 5 ml and cooling to 4 °C, 64 mg (0.08 mmol, 80%) of colorless needles were obtained.

^{1}H NMR (acetonitrile-d_3): δ = 2.11 (s, 3H, SCH_3), 3.90 (s, 3H, NCH_3), 4.17 (s, 2H, CH_2SCH_3), 7.45–7.53 (m, 2H, imidazole), 7.59–7.69 (m, 16H, 1H im. + 15H PPh_3), 7.87–7.91 (m, 1H, im.). ^{13}C NMR (acetonitrile-d_3, assignment based on DEPT 135-spectroscopy): δ = 16.40 (SCH_3), 29.84 (CH_2SCH_3), 31.97 (NCH_3), 112.37, 118.58 (C-5,6 imidazole), 125.41, 125.71 (C-4,7 im.), 129.20 (d, $J_{\text{C-P}}$ = 58.7 Hz, PPh_3), 130.62 (d, $J_{\text{C-P}}$ = 10.4 Hz, PPh_3), 133.50 (s, PPh_3), 135.14 (d, $J_{\text{C-P}}$ = 12.2 Hz, PPh_3), 135.65, 139.91 (C-3a,7a im.), 156.53 (C-2 im.). ^{31}P NMR (acetonitrile-d_3): δ = 30.01 (s, PPh_3), -143.89 (sept, $J_{\text{P-F}}$ = 706 Hz, PF_6).

$C_{28}H_{27}AuF_6N_2P_2S$ (796.48)
Calcd C 42.22 H 3.42 N 3.52%,
Found C 43.40 H 3.34 N 3.53%.

X-ray crystallography

Single crystals of $[(Ph_3P)Au(mmb)](PF_6)$ were grown by cooling a saturated solution in dichloromethane/n-pentane (4/1) at 4 °C. The dimensions of the crystal chosen were 0.08 x 0.08 x 0.2 mm.

Reflections were collected on an IPDS (Stoe) system at 295 K with graphite-monochromated Mo-Kα radiation. The structure was solved by direct methods and refined by full-matrix least-square calculations using the Shelxtl Version 5.1 [14]. There are two crystallographically independent ion pairs in the unit cell, differentiated by indices 1 and 2.

Anisotropic thermal parameters were refined for all non-hydrogen atoms. The hydrogen atoms were added to the structure model in calculated positions with isotropic temperature factors 20% (CH) or 50% (CH_3) higher than those of the corresponding carbon atoms. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 134342. Copies of the information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, Fax. (int. code) +44 (1223)336–033, or Email: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk.

Acknowledgements

This work has been supported by the Deutsche Forschungsgemeinschaft (DFG). We also thank Dr. F. Lissner for the crystallographic measurements.

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