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Mono- and dinuclear gold(I) thio- and selenocyanate complexes

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Dedicated to Prof. Martin Bennett

Abstract

Complexes of the type $(R_3P)AuSCN$ and $(R_3P)AuSeCN$ have been prepared in high yields from the corresponding chlorides $(R_3P)AuCl$ by treatment with KSCN or KSeCN, respectively, in a two-phase water/dichloromethane system. Crystal structure determinations revealed discrete monomeric molecules for the isomorphous thiocyanate and selenocyanate compounds with R = 2-MeC_6H_4. For R = ^{i}Pro there is only weak association into dimers via long Au–S contacts, but for $R_3 = Me_2PhP$ chain-like polymers are formed via short aurophilic interactions [Au–Au, 3.2334(2) and 3.2533(2) Å]. A monoclinic modification of $(Ph_3P)AuSCN$ was found, which shows a standard geometry of the molecules. An orthorhombic modification published previously featured a doubtful strongly distorted molecular geometry. All compounds of the type $(R_3P)AuS/SeCN$ can be converted into salts with dinuclear cations $\{[(R_3P)Au]_2S/SeCN\}^+Y^-$ on reaction with equimolar quantities of $[(R_3P)Au]^+Y^-$ ($Y = BF_4$, SbF_6) as confirmed by analytical and spectroscopic data. The S/SeCN units are found to be bridging the two metal atoms via the S/Se atoms. The tetrafluoroborates are less stable than the hexafluoroantimonates, and all selenocyanate complexes are markedly less stable thermally and more sensitive towards air and moisture than their sulfur counterparts.

Keywords: Selenocyanate complexes; Thiocyanate complexes; Gold

1. Introduction

Gold(I) pseudohalides are among the most important classes of gold compounds [1]. This is, particularly, true for gold(I) cyanides which are not only key intermediates for recovery and recycling of gold [2], but also for gold plating [3] and gold surface technology [4]. The cyanide anion $[CN]^-$ has the highest affinity for gold(I) and leads to the most dramatic changes in the electrochemical potential of gold in aqueous solution. In this respect, it exceeds even sulfide $[S]^{2-}$, hydrogensulfide $[SH]^-$ and thiocyanate anions $[SCN]^-$ which give rise to stability constants not very different from the cyanide extreme [5]. Gold extraction processes have also been probed with thiocyanate as a leaching agent, which may have technological and environmental advantages over cyanide [6], however, like technologies employing thiourea and thiosulfate, the thiocyanate process has never become a strong competitor of cyanide leaching.

Gold(I) thiocyanate complexes have also been investigated as chemotherapeutic agents, including mainly studies of the anti-tumor and anti-HIV activity, and cytotoxicity of several tertiary phosphine complexes of AuSCN [7]. These complexes may also be involved in the transformation of contemporary gold drugs like Auranofin® in the human body because of the almost ubiquitous presence of traces of cyanide and the metabolic generation of $[Au(CN)_2]^-$ [8]. The role and action of selenocyanate $[SeCN]^-$ has been studied much less, but the importance of selenium-dependent enzymes suggests that complexes of AuSeCN may well also play a significant role in physiological processes involving traces of gold [9,10].

The literature on the complexes of the type $(R_3P)AuSCN$ [11–27] is quite extensive, but for $(R_3P)AuSeCN$ [10,13,14,16] it remained rather limited (Table 1), and structural data are available only for isolated cases. As a continuation of recent studies [11],

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Table 1
Gold(I) thiocyanate and selenocyanate complexes with mono-, bi- and tridentate tertiary phosphine ligands

Complex	Literature
Monodentate ligands	
$(Me_3P)AuSCN$	[11–14]
$(Et_3P)AuSCN$	[12,15]
$[(^iPr)_3P]AuSCN$	[12], this work
$(Ph_3P)AuSCN$	[12–14,16–22], this work
$[(2\text{-}MeC_6H_4)_3P]AuSCN$	this work
$[(3\text{-}MeC_6H_4)_3P]AuSCN$	this work
$[(4\text{-}MeC_6H_4)_3P]AuSCN$	[17]
$[(4\text{-}ClC_6H_4)_3P]AuSCN$	[17,23]
$[(2\text{-}CN\text{–}C_2H_4)_3P]AuSCN$	[12]
$[(PhO)_3P]AuSCN$	[13,14]
$(Me_2PhP)AuSCN$	[24], this work
$(MePh_2P)AuSCN$	[24]
$(EtPh_2P)AuSCN$	[17,24]
$[(4\text{-}MeC_6H_4)Ph_2P]AuSCN$	[12]
$(Et_3P)AuSeCN$	[10]
$(Ph_3P)AuSeCN$	[13,14,16], this work
$[(2\text{-}MeC_6H_4)_3P]AuSeCN$	this work
$(Me_2PhP)AuSeCN$	this work
Bidentate ligands	
$NCSAu[(Ph_2P)\text{-}CH_2\text{-}(PPh_2)]AuSCN$	[24]
$NCSAu[(Ph_2P)\text{-}CH_2\text{-}CH_2\text{–}(PPh_2)]AuSCN$	[16,17,24]
$NCSAu[(Et_2P)\text{-}C_6H_4\text{-}(PEt_2)]AuSCN$	[25]
$NCSAu[(Ph_2P)\text{-}C_6H_4\text{-}(PPh_2)]AuSCN$	[25]
$NCSAu[(Ph_2P)\text{-}CH{=}CH\text{-}(PPh_2)]AuSCN$	[24]
$NCSAu[(Ph_2P)\text{-}C{\equiv}C\text{-}(PPh_2)]AuSCN$	[26]
$NCSeAu[(Ph_2P)\text{-}CH_2\text{-}CH_2\text{-}(PPh_2)]AuSeCN$	[16]
Tridentate ligands	
$NSCAu\{[(Ph_2P)\text{–}CH_2\text{–}[(PPh)AuSCN]\text{–}CH_2\text{–}(PPh_2)]\}\text{-}AuSCN$	[27]

Refs. [11,20] indicate structural characterization.

we, therefore, investigated a series of representative complexes, which were expected to provide more detailed structural data and information on the formation and general properties of such compounds. Particular attention was focused on dinuclear species in which the pseudohalide anion is in a bridging position between two metal atoms. Results of recent studies of the corresponding halide complexes have shown that these dinuclear compounds may aggregate further to give larger clusters [28–30].

2. Preparative results

In previous studies, the synthesis of complexes of the general type $(R_3P)AuSCN$ and $(R_3P)AuSeCN$ was carried out as a heterogeneous process in a non-aqueous solvent. As recently demonstrated [11,25,27], there is great advantage in a preparation in a two-phase system with an alkali thiocyanate dissolved in water and a (phosphine)gold(I) halide in dichloromethane. This convenient synthesis (Eqs. (1) and (2)) gives pure products as colourless solids in high yields.

$$(R_3P)AuCl + KSCN \rightarrow KCl + (R_3P)AuSCN \quad (1)$$

For **1**: R = Ph; **2**: R = 2-MeC_6H_4; **3**: R = 3-MeC_6H_4; **4**: $R_3 = Me_2Ph$; **5**: R = ^{i}Pro.

$$(R_3P)AuCl + KSeCN \rightarrow KCl + (R_3P)AuSeCN \quad (2)$$

For **6**: R = Ph; **7**: R = 2-MeC_6H_4; **8**: $R_3 = Me_2Ph$.

The thiocyanate compounds **1**–**3** with bulky triarylphosphines are very stable and show no decomposition at room temperature in the laboratory atmosphere and in daylight. The alkylphosphine thiocyanate complexes **4** and **5** are air-sensitive, but can be kept in sealed vessels at room temperature. By contrast, all selenocyanate complexes **6**–**8** are thermolabile as solids and in solution, and must be stored at low temperature in the dark. Exposed to air the compounds decompose rapidly with formation of red elemental selenium.

The compounds have been identified by elemental analyses, mass spectrometry, and their IR and NMR spectroscopic characteristics. The thiocyanates **1**–**5** show intense absorptions for the ν(CN) stretching vibration shifted very significantly to higher wavenumbers (2110–2130 cm^{-1}) as compared with free $[SCN]^-$: 2066 cm^{-1} [31]. This is indicative of binding of the gold atom solely to the sulfur/selenium end of the anion. A weak band detected for all thiocyanate complexes at 2053–2075 cm^{-1} can be assigned to a combination mode, which is not observed for the selenocyanate complexes **6**–**8** owing to the larger mass of selenium. The NMR spectra show only one set of sharp resonances for the PR_3 ligand independent of temperature, which rules out any equilibrium of the type shown in Eq. (3). The ^{31}P signals of the thiocyanates **1**–**5** are shifted to lower fields by about 5 ppm as compared with the corresponding chloride complexes, while for the selenocyanates **6**–**8** an additional low-field shift of only less than 1.5 ppm is observed. The ^{13}C signals of the anions were not detected.

$$2(R_3P)AuSCN \rightleftarrows [(R_3P)_2Au]^+[Au(SCN)_2]^- \quad (3)$$

The FAB mass spectra of all complexes showed the protonated molecular ion, but the ions of highest abundance were the fragments $[(R_3P)Au]^+$ and the redistribution products $[(R_3P)_2Au]^+$ and $\{[(R_3P)Au]_2S/SeCN\}^+$. This observation is in agreement with results obtained with halide complexes $[(R_3P)AuX]$ (X = Cl, Br, I) where cations $\{[(R_3P)Au]_2X\}^+$ are observed with high abundance. The results suggest that dinuclear thio/selenocyanate complexes are readily formed and of high stability as isolated species in the gas phase.

Preparative attempts confirmed these expectations. Treatment of compounds $(R_3P)AuS/SeCN$ with equimolar quantities of $[(R_3P)Au]BF_4$ or $[(R_3P)Au]SbF_6$—prepared in situ—in dichloromethane at −78 °C gave

the dinuclear adducts in high yield (Eqs. (4) and (5)).

$$(R_3P)AuSCN + [(R_3P)Au]Y \rightarrow \{[(R_3P)Au]_2SCN\}^+Y^- \quad (4)$$

For **9**: R = Ph, Y = BF_4; **10**: R = Ph, Y = SbF_6; **11**: R = 2-MeC_6H_4, Y = SbF_6; **12**: R = 3-MeC_6H_4, Y = SbF_6; **13**: R_3 = Me_2Ph; Y = SbF_6; **14**: R = ^{i}Pro, Y = SbF_6.

$$(R_3P)AuSeCN + [(R_3P)Au]SbF_6 \rightarrow \{[(R_3P)Au]_2SeCN\}^+[SbF_6]^- \quad (5)$$

For **15**: R = Ph; **16**: R_3 = Me_2P; **17**: R = 2-MeC_6H_4.

The *thiocyanates* are colourless solids which are soluble in polar solvents like dichloromethane, tetrahydrofuran or chlorobenzene, but insoluble in pentane or diethylether. The tetrafluoroborate salt **9** proved to be much less stable as a solid and in solution against air and light than the hexafluoroantimonate **10** and, therefore, for all other preparations only the hexafluoroantimonates were chosen (**10**–**17**). The sterically protected compounds **11** and **12** are again found to be most stable and the solids can be handled in air and daylight. However, solutions are very unstable and decomposition is observed already after a few minutes at room temperature.

The *selenocyanates* **15**–**17** are very unstable and were found to decompose rapidly already above −40 °C. The compounds were characterized only tentatively on the basis of their solution NMR and solid state IR data (see Section 4). Red selenium and yellow gold(I) cyanide appear as the decomposition products in solution and in solids isolated from the reaction mixture by evaporation of all volatiles at −78 °C.

Solutions of compounds **9**–**14** in CD_2Cl_2 at −50 °C show ^{31}P singlet resonances which are shifted upfield from the signals of the precursor molecules **1**–**5** by approximately 3.6 (**9**, **10**), 4.1 (**11**), 2.2 (**12**, **14**) and 4.4 ppm (**13**). The effects observed for the resonances of the organic substituents are only marginal. The IR spectra exhibit shifts of the ν(CN) stretching frequency to higher wavenumbers by up to 35 cm^{-1} (**9**–**13**). This displacement is in agreement with a model in which the sulfur atom of the thiocyanate group is η^2-coordinated to two metal atoms. For N-coordination of the second gold atom a shift in the opposite direction is to be expected. The ^{31}P NMR and IR data of **15** are similar to those of **10** suggesting analogous effects of the complexation.

Mass spectra (FAB) could only be obtained for the compounds with aryl substituents (**9**–**12**). The spectra show the cations $\{[(R_3P)Au]_2SCN\}^+$ as the peaks of highest mass followed by $[(R_3P)_2Au]^+$ and $[(R_3P)Au]^+$. It should be remembered that the same series of peaks was also observed for the precursor molecules **1**–**3**, but with entirely different intensity ratios. The dinuclear cation is the dominant species in the high-mass region of the spectra of the hexafluoroantimonate salts, while for the mononuclear compounds it was only a minor component probably formed upon bombardment and ionization of the samples.

Although no single crystals could be grown for any of the tetrafluoroborate or hexafluoroantimonate salts, the spectroscopic and analytical data provide sufficient evidence for the products proposed in Eqs. (4) and (5). The results are also in agreement with previous work, where a different preparative approach had been chosen [22,28–30].

3. Structural investigations

(Triphenylphosphine)gold thiocyanate (**1**) was obtained in an orthorhombic form in a previous study by Barron et al. [20]. The structure was solved with low precision and gave a molecular geometry with unexpected distorsions, in particular an angle S–C–N of 161(3)° and a distance S–C of 1.36(2) Å.

In our own experiments a monoclinic form, space group $P2_1/c$ ($Z = 2$), was isolated from an solution containing $(Ph_3P)AuCl$. The structure could be refined on a perfectly satisfactory level and gave a molecular geometry, which meets the expectations. The distances Au1–P1, Au1–S1 and S1–C1 are 2.2542(13), 2.3312(15) and 1.614(9) Å, respectively, are in the range established by earlier investigations of (phosphine)gold sulfur compounds. The angle S1–C1–N1 of 177.1(1)° is close to linear.

The molecules are loosely aggregated into pairs through long Au–S contacts (Au1–S1′, 3.495 Å) which are reminiscent of the structure of $(Me_3P)AuSCN$ [11] (Fig. 1).

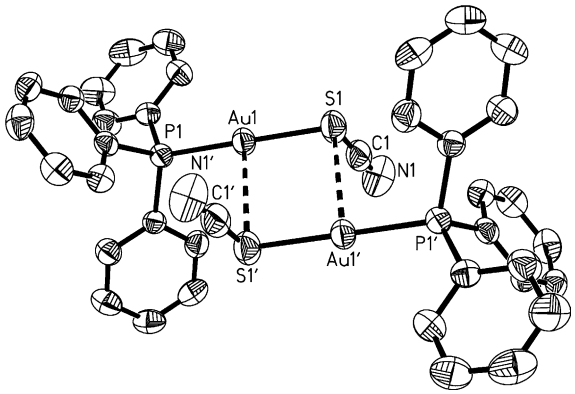

Fig. 1. Molecular structure of $(Ph_3P)AuSCN$ (**1**) (ORTEP, 50% probability ellipsoids). The monomers are loosely aggregated into dimers with long Au-S contacts of 3.495 Å. Selected structural parameters: Au-S 2.3312(15), Au-P 2.2542(13), S-C 1.614(9) and C-N 1.203(10) Å, P-Au-S 177.88(6)°, Au-S-C 95.4(2)° and S-C-N 177.4(6)°.

The two complexes **2** and **7** with bulky $(2\text{-}MeC_6H_4)_3P$ ligands are expected to have simple mononuclear structures because steric hindrance rules out any close approach of the metal atoms. This expectation is confirmed by the single crystal structure investigations. The orthorhombic crystals of the sulfur (**2**) and selenium compound (**7**) are isomorphous of space group *Pbca* ($Z = 8$) with very similar unit cell geometries (Table 2). The lattices contain isolated molecules (Figs. 2 and 3) with no sub-van der Waals contacts. The tertiary phosphines have a propeller-type arrangement of the three *ortho*-tolyl groups very common for this ligand in any of its complexes. The configuration of the metal atom is close to linear with P1–Au1–S1 176.90(3)° and P1–Au1–Se1 176.90(2)°. The angles at the chalkogen atoms are acute with Au1–S1–C1 98.75(11)° and Au1–Se1–C1 96.73(11)° while the angle at the internal carbon atom of the pseudohalide group is again close to linear: S1–C1–N1 177.1(3)° and Se1–C1–N1 177.2(3)°. Significant differences are found for the distances Au1–S1 2.3256(8)/S1–C1 1.681(3) and Au1–Se1 2.4259(3)/Se1–C1 1.843(4) Å, which reflect the increasing covalent radius of selenium as compared with sulfur. Note that the differences (0.100 for Au–S/Se and 0.162 Å for S/Se–C) are not the same. It appears that the Au–Se bond is, particularly, short which may reflect the high affinity of gold for selenium (and tellurium!). All other dimensions in **2** and **7** show only minor variations.

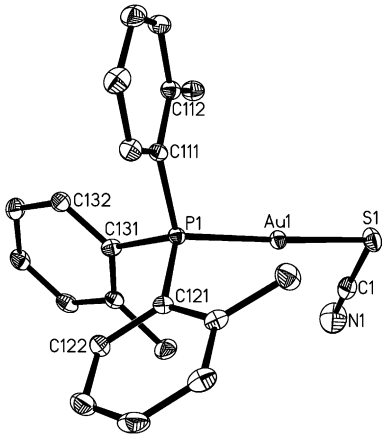

Fig. 2. Molecular structure of $[(2\text{-}MeC_6H_4)_3P]AuSCN$ (**2**) (ORTEP, 50% probability ellipsoids). Selected structural parameters: Au-S 2.3256(8), Au-P 2.2726(7), S-C 1.681(3) and C-N 1.147(4) Å, P-Au-S 176.90(3)°, Au-S-C 98.75(11)° and S-C-N 177.1(3)°.

Table 2
Crystal data, data collection, and structure refinement

	$Ph_3PAuSCN$ (**1**)	$(o\text{-Tol})_3PAuSCN$ (**2**)	$Me_2PhPAuSCN$ (**4**)	$(^iPro)_3PAuSCN$ (**5**)	$(o\text{-Tol})_3PAuSeCN$ (**7**)
Crystal data					
Empirical formula	$C_{19}H_{15}AuNPS$	$C_{22}H_{21}AuNPS$	$C_9H_{11}AuNPS$	$C_{10}H_{21}AuNPS$	$C_{22}H_{21}AuNPSe$
M_r	516.96	559.39	393.18	415.27	606.29
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	*Pbca*	$P2_1/n$	$P2_1/c$	*Pbca*
a (Å)	9.3287(3)	14.9490(1)	11.6485(1)	7.9085(1)	15.0130(1)
b (Å)	17.3955(5)	16.2360(1)	12.2737(1)	8.4179(1)	16.2840(1)
c (Å)	11.4669(4)	16.1510(2)	16.3318(2)	21.1214(3)	16.3170(2)
α (°)	90	90	90	90	90
β (°)	105.889(1)	90	105.809(1)	99.271(1)	90
γ (°)	90	90	90	90	90
V (Å^3)	1789.7(1)	3920.0(1)	2246.7(1)	1387.8(1)	3988.5(1)
ρ_{calc} (g cm^{-3})	1.920	1.896	2.325	1.988	2.019
Z	4	8	8	4	8
$F(0\,0\,0)$	984	2160	1456	792	2304
μ(Mo Kα) (cm^{-1})	84.24	76.99	133.79	108.35	92.88
Data collection					
T (K)	−130	−130	−130	−130	−130
Measured reflections	31160	159555	86484	36402	102754
Unique reflections	3963 [$R_{int} = 0.049$]	5810 [$R_{int} = 0.054$]	6125 [$R_{int} = 0.052$]	3023 [$R_{int} = 0.044$]	4391 [$R_{int} = 0.052$]
Absorption correction	DELABS	DELABS	DELABS	DELABS	DELABS
T_{min}/T_{max}	0.461/0.824	0.447/0.818	0.439/0.814	0.428/0.809	0.488/0.836
Refinement					
Refined parameters	208	319	235	127	235
Final R values [$I \geq 2\sigma(I)$]					
R_1	0.0346	0.0251	0.0294	0.0251	0.0215
wR_2[a]	0.0814	0.0597	0.0722	0.0647	0.0519
(Shift/error)$_{max}$	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Max./min., ρ_{fin} (e Å^{-3})	2.210/−1.398	1.639/−0.932	2.879/−1.744	2.554/−1.125	0.979/−0.636

[a] $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$; $a = 0.0000$ (**1**), 0.0107 (**2**), 0.0364 (**4**), 0.0234 (**5**), 0.0073 (**7**); $b = 4.49$ (**1**), 8.58 (**2**), 4.29 (**4**), 3.06 (**5**), 8.90 (**7**).

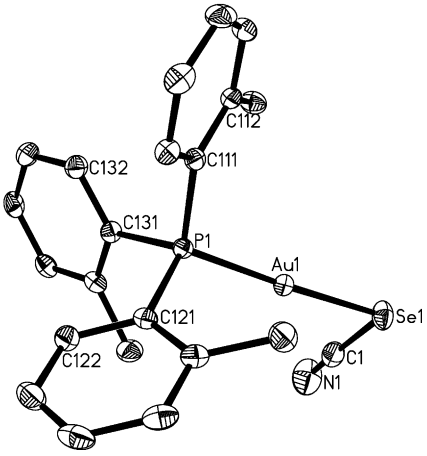

Fig. 3. Molecular structure of $[(2\text{-}MeC_6H_4)_3P]AuSeCN$ (**7**) (ORTEP, 50% probability ellipsoids). Selected structural parameters: Au-Se 2.4259(3), Au-P 2.2781(8), Se-C 1.843(4) and C-N 1.134(5) Å; P-Au-Se 176.90(2)°, Au-Se-C 96.73(11)° and Se-C-N 177.2(3)°.

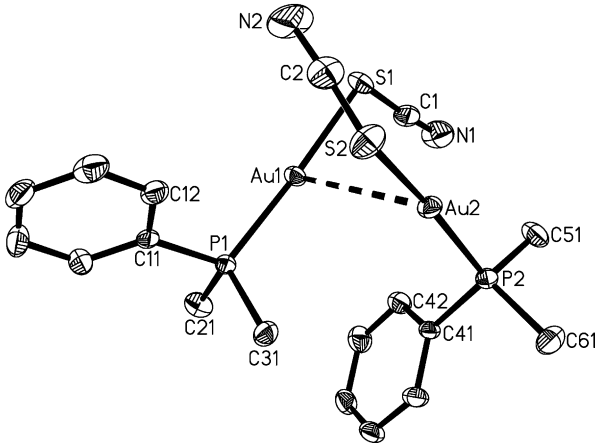

Fig. 5. Molecular structure of $(Me_2PhP)AuSCN$ (**4**) (ORTEP, 50% probability ellipsoids). The monomers are aggregated into dimers through short aurophilic contacts [Au1-Au2, 3.2533(2) Å]. Selected structural parameters: Au1-S1 2.3423(10), Au2-S2 2.3554(13), Au1-P1 2.2618(10), Au2-P2 2.2681(11), S1-C1 1.675(5), S2-C2 1.638(6), C1-N1 1.141(7) and C2-N2 1.192(7) Å; P1-Au1-S1 176.10(4)°, P2-Au2-S2 169.89(4)°, Au1-S1-C1 101.44(16)°, Au2-S2-C2 105.90(19)°, S1-C1-N1 176.7(5)° and S2-C2-N2 166.9(6)°.

Crystals of the tri(^{i}propyl)phosphine complex **5** are monoclinic, space group $P2_1/c$, with $Z = 4$ formula units in the unit cell. The individual molecules are not completely separated and feature distant intermolecular contacts between the gold and sulfur atoms (Fig. 4; Au1–S1′ 3.738 Å). The two monomers in the aggregate are related by a center of inversion. This mode of association is again reminiscent of the structure of $(Me_3P)AuSCN$ [11]. The angles P1–Au1–S1 [179.72(4)°] and S1–C1–N1 [177.9(4)°] are almost linear, but the chain of atoms is strongly bent at the sulfur atom: Au1–S1–C1 99.51(15)°. All other details deserve no special comment.

Crystals of the dimethylphenylphosphine complex **4** are also monoclinic, space group $P2_1/n$, with $Z = 8$ formula units in the unit cell. The asymmetric unit contains two independent molecules aggregated via an aurophilic contact to form a dimer as shown in Fig. 5. These dimers are further aggregated to give chains as illustrated in Fig. 6. Clearly, the strongly reduced steric bulk of the phosphine Me_2PhP (as compared with **1**, **2**, **5**, and **7**,above) gives sufficient room for close contacts between the monomers. Along the meandering chains of metal atoms there are alternating (but very similar) intra- and inter-dimer Au1–Au2 distances of 3.2334(2) and 3.2533(2) Å. The Au–Au–Au angles along the chain of gold atoms are 159.942(5)° at Au1 and 148.050(5)° at Au2 with a torsional angle Au2′–Au1–Au2–Au1′ of 47.847(18)°. The internal dimensions of the individual molecules show no anomalies except for a striking difference (10°) in the S–C–N angles for the two independent molecules: S1–C1–N1 176.7(5), S2–C2–N2 166.9(6)°. The angles Au1–S1–C1 101.4(2)° and Au2–S2–C2 105.9(2)° in **4** differ much less (4.5°), but this difference may still be responsible for the variation in the neighbouring S–C–N angle. There is no evidence for unusual differences in intermolecular contacts of the two thiocyanate groups in the lattice (Fig. 5).

In the family of (phosphine)gold thiocyanates, $(Me_2PhP)AuSCN$ is only the third case where aurophilic

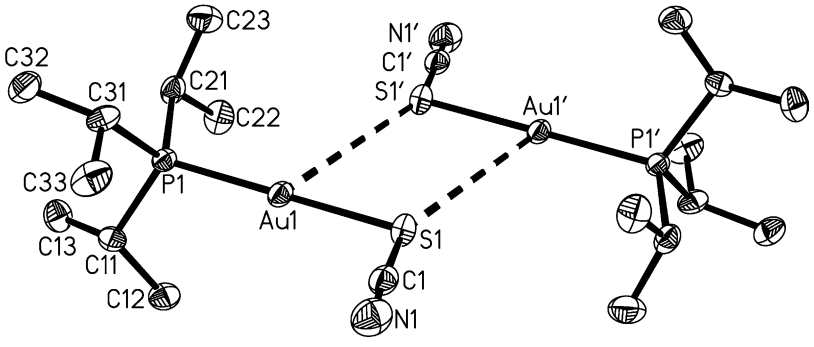

Fig. 4. Molecular structure of $[(Me_2CH)_3P]AuSCN$ (**5**) (ORTEP, 50% probability ellipsoids). The monomers are aggregated loosely into dimers with long Au-S′ contacts of 3.738(6) Å. Selected structural parameters: Au-S 2.3276(10), Au-P 2.2696(10), S-C 1.691(5) and C-N 1.151(6) Å; P-Au-S 179.72(4)°, Au-S-C 99.51(15)° and S-C-N 177.9(4)°.

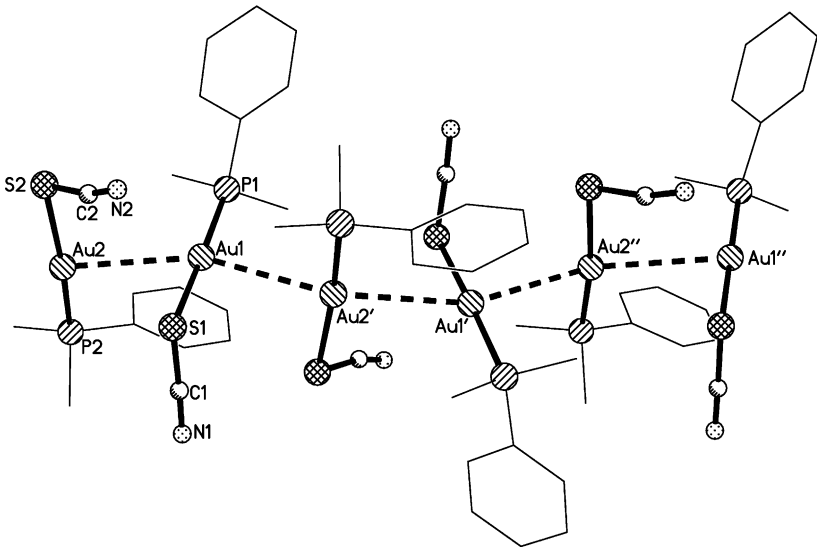

Fig. 6. Aggregation of the dimers shown in Fig. 5 into chains via aurophilic contacts [Au1-Au2′ 3.2334(2) Å]. Angles and torsional angles of the chain: Au2-Au1-Au2′ 159.942(5)°, Au1-Au2-Au1′ 148.050(5)°, Au2′-Au1-Au2-Au1′ 47.847(18)°.

interactions determine the arrangement of the molecules in the solid state. A cyclic aggregate was discovered by Bennett et al. [25].

4. Experimental

4.1. General

All experiments were routinely carried out in an atmosphere of dry nitrogen. Solvents and glassware were dried and saturated/filled with nitrogen. Standard equipment was used throughout. The AuCl complexes were prepared by published methods [32–37]. All NMR spectra (δ in [ppm], J in [Hz]) were recorded in CD_2Cl_2 at 23 °C unless otherwise stated.

4.2. (Triphenylphosphine)gold thiocyanate (*1*) [20]

Solutions of $(Ph_3P)AuCl$ (300 mg, 0.61 mmol) in dichloromethane (12 ml) and of KSCN (127 mg, 1.29 mmol) in water (10 ml) were mixed and stirred vigorously for 3 h at 20 °C. The aqueous phase was then separated from the organic phase and extracted three times with 5 ml portions of CH_2Cl_2. The combined organic phases were washed three times with 5 ml portions of water and dried over $MgSO_4$. The solvent was evaporated in a vacuum until a precipitate appeared. By addition of pentane (50 ml) and cooling to −30 °C overnight the precipitation is complete. After filtration and drying in a vacuum the product was recrystallized from dichloromethane/pentane. The colourless solid is stable to air and light, and soluble in CH_2Cl_2, tetrahydrofuran and chlorobenzene, but insoluble in *n*-pentane and diethylether. Yield, 260 mg (83%); m.p., 169 °C. ^{1}H NMR: $\delta = 7.52–7.58$ [m, Ph]. $^{13}C\{^1H\}$ NMR: $\delta = 134.6$ [d, $^2J(C,P) = 13.5$ Hz, C2/6], 132.6 [s, C4], 129.8 [d, $^3J(C,P) = 11.9$ Hz, C3/5], 128.3 [d, $^1J(C,P) = 62.8$ Hz, C1]. $^{31}P\{^1H\}$ NMR: $\delta = 37.9$ [s, PPh_3]. IR (KBr): 2130 cm^{-1}, s, 2075 cm^{-1}, w, ν(CN). MS (FAB): $m/z = 977$ (48.6%) $\{[(Ph_3P)Au]_2SCN\}^+$, 721 (28.6) $[(Ph_3P)_2Au]^+$, 518 (15.6) $[M+1]^+$, 459 (100) $[(Ph_3P)Au]^+$, 262 (6.3) $[Ph_3P]^+$. Anal. Calc. for $C_{19}H_{15}AuNPS$ (517.34 g mol^{-1}): C, 44.1; H, 2.9; N, 2.7. Found: C, 44.0; H, 2.9; N 2.7%.

4.3. [Tri(2-methylphenyl)phosphine]gold thiocyanate (*2*)

Following the same procedure using 300 mg (0.57 mmol) of $[(2\text{-}MeC_6H_4)_3P]AuCl$ and 112 mg (1.14 mmol) of KSCN; Yield, 255 mg (80%); m.p. (dec.), 225 °C. ^{1}H NMR: $\delta = 6.85–7.53$ [m, 12H, C_6H_4], 2.70 [s, 9H, Me]. $^{13}C\{^1H\}$ NMR: $\delta = 143.3$ [d, $^2J(C,P) = 14.6$ Hz, C2], 134.1 [d, $^2J(C,P) = 9.2$ Hz, C6], 132.9 [d, $^3J(C,P) = 8.5$ Hz, C5], 132.6 [s, C4], 127.3 [d, $^3J(C,P) = 10.0$ Hz, C3], 125.2 [d, $^1J(C,P) = 59.9$ Hz, C1], 23.5 [d, $^3J(C,P) = 11.5$ Hz, Me]. $^{31}P\{^1H\}$ NMR: $\delta = 13.1$ [s, P(*o*-tol)$_3$]. IR (KBr): 2120 cm^{-1}, s, 2071 cm^{-1}, w, ν(CN). MS (FAB): $m/z = 1061$ (7.3%) $\{[(o\text{-tol})_3PAu]_2SCN\}^+$, 806 (15.6) $\{[(o\text{-tol})_3P]_2Au\}^+$, 560 (53.1) $[M+1]^+$, 501 (100) $\{[(o\text{-tol})_3P]Au\}^+$. Anal. Calc. for $C_{22}H_{21}AuNPS$ (559.42 g mol^{-1}): C, 47.2; H, 3.8; N, 2.5; S, 5.7. Found: C, 46.9; H, 3.8; N, 2.5; S, 5.8%.

4.4. [Tri(3-methylphenyl)phosphine]gold thiocyanate (*3*)

Following the same procedure using 250 mg (0.47 mmol) of $[(3\text{-}MeC_6H_4)_3P]AuCl$ and 92 mg (0.94 mmol)

of KSCN; Yield, 212 mg (81%); m.p. (dec.), 119 °C. ^{1}H NMR: $\delta = 7.20–7.45$ [m, 12H, C_6H_4], 2.36 [s, 9H, Me]. $^{13}C\{^1H\}$ NMR: $\delta = 139.9$ [d, $^2J(C,P) = 12.4$ Hz, C2], 135.0 [d, $^2J(C,P) = 14.5$ Hz, C6], 133.3 [d, $^4J(C,P) = 2.6$ Hz, C4], 131.6 [d, $^3J(C,P) = 13.0$ Hz, C3], 129.5 [d, $^3J(C,P) = 11.9$ Hz, C5], 128.7 [d, $^1J(C,P) = 60.2$ Hz, C1], 21.6 [s, Me]. $^{31}P\{^1H\}$ NMR: $\delta = 37.8$ [s, P(*m*-tol)$_3$]. IR (KBr): 2120 cm^{-1}, s, 2070 cm^{-1}, w, ν(CN). MS (FAB): *m*/*z* cations as for **2** with relative intensities 44.0, 21.3, 11.3, and 100%. Elemental analysis: Found: C, 47.0; H, 3.8; N, 2.5; S 5.5% (cf. **2**).

4.5. (Dimethylphenylphosphine)gold thiocyanate (**4**)

Following the same procedure using 400 mg (1.08 mmol) of (Me_2PhP)AuCl and 212 mg (2.16 mmol) KSCN; Yield, 314 mg (75%); m.p. (dec.), 135 °C. ^{1}H NMR: $\delta = 7.53–7.73$ [m, 5H, Ph], 1.91 [d, $^2J(H,P) = 10.8$ Hz, 6H, Me]. $^{13}C\{^1H\}$ NMR: $\delta = 132.6$ [d, $^4J(C,P) = 2.3$ Hz, C4], 132.2 [d, $^2J(C,P) = 13.8$ Hz, C2/6], 129.8 [d, $^3J(C,P) = 11.5$ Hz, C3/5], C1 not detected, 15.8 [d, $^1J(C,P) = 37.7$ Hz, Me]. $^{31}P\{^1H\}$ NMR: $\delta = 9.8$ [s, PMe_2Ph]. IR (KBr): 2112 cm^{-1}, s, 2053 cm^{-1}, w, ν(CN). MS (FAB): *m*/*z* = 728 (18.4%) {[(Me_2PhP)-Au]$_2$SCN}$^+$, 473 (7.9) [(Me_2PhP)$_2$Au]$^+$, 394 (74.6) [M+1]$^+$, 335 (100) [(Me_2PhP)Au]$^+$. Anal. Calc. for $C_9H_{11}AuNPS$ (393.20 g mol^{-1}): C, 27.5; H, 2.8; N, 3.6; S, 8.2. Found: C, 27.4; H, 2.8; N, 3.6; S 8.0%.

4.6. [Tri(^{i}propyl)phosphine]gold thiocyanate (**5**)

Following the same procedure using 200 mg (0.51 mmol) of [(^{i}Pro)$_3$P]AuCl and 100 mg (1.02 mmol) of KSCN; Yield, 165 mg (78%); m.p., 73 °C. ^{1}H NMR: $\delta = 2.35$ [sept, $^3J(H,H) = 7.4$ Hz, 1H, CH], 1.34 [d, $^3J(H,H) = 7.4$ Hz, 6H, Me]. $^{13}C\{^1H\}$ NMR: $\delta = 24.3$ [d, $^2J(C,P) = 29.2$ Hz, CH], 20.6 [s, Me]. $^{31}P\{^1H\}$ NMR: $\delta = 69.6$ [s, P(^{i}Pro)$_3$]. IR (KBr): 2125 cm^{-1}, s, 2075 cm^{-1}, w, ν(CN). MS (FAB): *m*/*z* = 772 (56.7%) {[(^{i}Pro)$_3$PAu]$_2$SCN}$^+$, 416 (9.1) [M+1]$^+$, 357 (100) {[(^{i}Pro)$_3$P]Au}$^+$. Anal. Calc. for $C_{10}H_{21}AuNPS$ (415.29 g mol^{-1}): C, 28.9; H, 5.1; N, 3.4; S, 7.7. Found: C, 28.8; H, 5.1; N, 3.4; S, 7.6%.

4.7. (Triphenylphosphine)gold selenocyanate (**6**)

Following the same procedure using 300 mg (0.60 mmol) of (Ph_3P)AuCl and 130 mg (0.90 mmol) of KSeCN; Yield, 254 mg (75%). The solid product and its solutions decompose slowly at room temperature. ^{1}H NMR: $\delta = 7.53–7.59$ [m, Ph]. $^{13}C\{^1H\}$ NMR: $\delta = 134.6$ [d, $^2J(C,P) = 13.5$ Hz, C2/6], 132.5 [s, C4], 129.3 [s, C3/5], C1 not detected. $^{31}P\{^1H\}$ NMR: $\delta = 38.8$ [s, PPh_3]. IR (KBr): 2120 cm^{-1}, s, ν(CN). MS (FAB): *m*/*z* = 1024 (2.0%) {[(Ph_3P)Au]$_2$SeCN}$^+$, 721 (8.3) [(Ph_3P)$_2$Au]$^+$, 566 (12.4) [M+1]$^+$, 459 (100) [(Ph_3P)Au]$^+$. Anal. Calc. for $C_{19}H_{15}AuNPSe$ (564.24 g mol^{-1}): C, 40.5; H, 2.7; N, 2.5. Found: C, 40.9; H, 2.9; N, 2.3%.

4.8. [Tri(2-methylphenyl)phosphine]gold selenocyanate (**7**)

Following the same procedure using 250 mg (0.47 mmol) [(2-MeC_6H_4)$_3$P]AuCl and 102 mg (0.70 mmol) of KSeCN; Yield, 231 mg (81%); m.p. (dec.), 110 °C. ^{1}H NMR: $\delta = 6.90–7.52$ [m, 12H, C_6H_4], 2.71 [s, 9H, Me]. $^{13}C\{^1H\}$ NMR: $\delta = 143.3$ [d, $^2J(C,P) = 12.3$ Hz, C2], 134.1 [d, $^2J(C,P) = 9.2$ Hz, C6], 132.8 [d, $^3J(C,P) = 8.5$ Hz, C5], 132.5 [s, C4], 127.3 [d, $^3J(C,P) = 10.0$ Hz, C3], 125.6 [d, $^1J(C,P) = 59.9$ Hz, C1], 23.5 [d, $^3J(C,P) = 7.8$ Hz, Me]. $^{31}P\{^1H\}$ NMR: $\delta = 15.6$ [s, P(*o*-tol)$_3$]. IR (KBr): 2127 cm^{-1}, s, ν(CN). MS (FAB): *m*/*z* = 805 (26.0%) {[(*o*-tol)$_3$P]$_2$Au}$^+$, 608 (36.3) [M+1]$^+$, 501 (100) {[(*o*-tol)$_3$P]Au}$^+$. Anal. Calc. for $C_{22}H_{21}AuNPSe$ (606.32 g mol^{-1}): C, 43.6; H, 3.5; N, 2.3. Found: C, 42.9; H, 3.6; N, 2.2%.

4.9. (Dimethylphenylphosphine)gold selenocyanate (**8**)

Following the same procedure using 200 mg (0.54 mmol) of (Me_2PhP)AuCl and 117 mg (0.81 mmol) of KSeCN; Yield, 181 mg (76%). The solid product and its solutions decompose at room temperature. ^{1}H NMR: $\delta = 7.51–7.95$ [m, 5H, Ph], 1.87 [d, $^2J(H,P) = 10.6$ Hz, 6H, Me]. $^{13}C\{^1H\}$ NMR: $\delta = 132.1$ [d, $^4J(C,P) = 2.4$ Hz, C4], 132.0 [d, $^2J(C,P) = 13.5$ Hz, C2/6], 129.7 [d, $^3J(C,P) = 11.4$ Hz, C3/5], C1 not detected, 15.8 [d, $^1J(C,P) = 36.8$ Hz, Me]. $^{31}P\{^1H\}$ NMR: $\delta = 11.0$ [s, PMe_2Ph]. IR (KBr): 2114 cm^{-1}, s, ν(CN). MS (FAB): *m*/*z* = 776 (5.1%) {[(Me_2PhP)Au]$_2$SeCN}$^+$, 553 (40.2) [(Me_2PhPSe)Au]$^+$, 473 (17.5) [(Me_2PhP)$_2$Au]$^+$, 442 (16.2) [M+1]$^+$, 335 (100) [(Me_2PhP)Au]$^+$. Anal. Calc. for $C_9H_{11}AuNPSe$ (440.10 g mol^{-1}): C, 24.6; H, 2.5; N, 3.2. Found: C, 25.4; H, 2.8; N, 2.9%.

4.10. (μ-Thiocyanato)-bis[(triphenylphosphine)gold] tetrafluoroborate (**9**) and hexafluoroantimonate (**10**), and (μ-selenocyanato)-bis[(triphenylphosphine)gold] hexafluoroantimonate (**15**)

100 mg (0.20 mmol) of (Ph_3P)AuCl is treated with 43 mg (0.22 mol) of $AgBF_4$ in CH_2Cl_2 (15 ml) at −78 °C for 30 min. The cold solution is filtered and added to a solution of 103 mg (0.20 mmol) of (Ph_3P)AuSCN in 10 ml of the same solvent. The reaction mixture is protected against light and stirred for 3 h at −78 °C. Subsequently, the solvent is evaporated in a vacuum to a volume of approximately 3 ml and cold pentane is added (25 ml) at −30 °C to precipitate the product (**9**), which is filtered and dried in a vacuum. Yield, 138 mg (65%); slow dec. above −10 °C.

The same reaction with 76 mg (0.22 mmol) of $AgSbF_6$ gives **10** in a yield of 177 mg (73%). This product is unstable above 20 °C.

The same reaction with $(Ph_3P)AuSeCN$ (112 mg, 0.20 mmol) gives a very unstable product **15** which decomposes slowly at −30 °C. The yield was not determined and no elemental analysis could be obtained.

The solution NMR spectra of **9** and **10** (in CD_2Cl_2) are very similar and only the complete data for **10** are given. ^{1}H NMR: $\delta = 7.46$–7.73 [m, Ph]. $^{13}C\{^1H\}$ NMR: $\delta = 133.8$ [d, $^2J(C,P) = 13.5$ Hz, C2/6], 132.4 [d, $^4J(C,P) = 2.6$ Hz, C4], 129.3 [d, $^3J(C,P) = 12.5$ Hz, C3/5], 126.8 [d, $^1J(C,P) = 64.3$ Hz, C1]. $^{31}P\{^1H\}$ NMR (−50 °C): $\delta = 34.2$ [s, PPh_3]. **9**: ^{11}B NMR: $\delta = -1.08$ [s, BF_4]. **15**: $^{31}P\{^1H\}$ NMR: $\delta = 35.4$ [s, PPh_3]. IR (KBr) **9**: 2155 cm^{-1}, s, 2122 cm^{-1}, w, 2070 cm^{-1}, vw, ν(CN); 1053 cm^{-1}, vs, ν(BF). **10**: 2154 cm^{-1}, s, 2133 cm^{-1}, w, 2080 cm^{-1}, vw, ν(CN); 656 cm^{-1}, vs, ν(SbF). **15**: 2155 cm^{-1}, s, 2122 cm^{-1}, w, ν(CN); 648 cm^{-1}, vs, ν(SbF).

MS (FAB) **9/10**: $m/z = 977$ (43.9/54.2%) $\{[(Ph_3P)Au]_2SCN\}^+$, 459 (100) $[(Ph_3P)Au]^+$.

Anal. Calc. for $C_{37}H_{30}Au_2BF_4NP_2S$ (**9**) (1063.40 g mol^{-1}): C, 41.8; H, 2.8; N, 1.3. Found: C, 43.6; H, 3.2; N, 1.1%. Anal. Calc. for $C_{37}H_{30}Au_2F_6NP_2SSb$ (**10**) (1212.34 g mol^{-1}): C, 36.7; H, 2.5; N, 1.1. Found: C, 37.2; H, 2.6; N, 1.0%.

4.11. (μ-Thiocyanato)-bis{[tri(2- and 3-methylphenyl)-phosphine]gold} hexafluoroantimonate (**11**) and (**12**)

Following the procedure given for **10** using [(2-/3-$MeC_6H_4)_3P$]AuCl (96 mg, 0.18 mmol), $AgSbF_6$ (80 mg, 0.23 mmol) and [(2-/3-$MeC_6H_4)_3P$]AuSCN (100 mg, 0.18 mmol) gave yields of 196/201 mg (84/86%) for **11/12**. Both compounds decompose slowly at ambient temperature.

11: ^{1}H NMR: $\delta = 6.93$–7.59 [m, 24H, C_6H_4], 2.64 [s, 18H, Me]; $^{13}C\{^1H\}$ NMR: $\delta = 143.3$ [d, $^2J(C,P) = 12.8$ Hz, C2], 134.2 [d, $^2J(C,P) = 8.5$ Hz, C6], 133.0 [d, $^3J(C,P) = 7.3$ Hz, C5], 132.9 [s, C4], 127.3 [d, $^3J(C,P) = 10.0$ Hz, C3], C1 not detected, 23.4 [d, $^3J(C,P) = 12.3$ Hz, Me]; $^{31}P\{^1H\}$ NMR (−50 °C): $\delta =$ 9.2 [s, P(*o*-tol)$_3$]. IR (KBr): 2158 cm^{-1}, s, 2124 cm^{-1}, w, 2075 cm^{-1}, vw, ν(CN); 656 cm^{-1}, vs, ν(SbF). MS (FAB): $m/z = 1061$ (95.2%) $\{[(o\text{-tol})_3PAu]_2SCN\}^+$, 805 (18.1) $\{[(o\text{-tol})_3P]_2Au\}^+$, 501 (100) $[(o\text{-tol})_3PAu]^+$. Anal. Calc. for $C_{43}H_{42}Au_2F_6NP_2SSb$ (1296.50 g mol^{-1}): C, 39.8; H, 3.3; N, 1.1. Found: C, 41.8; H, 3.5; N, 1.0%.

12: ^{1}H NMR: $\delta = 7.20$–7.45 [m, 24H, C_6H_4], 2.35 [s, 18H, Me]. $^{13}C\{^1H\}$ NMR: $\delta = 140.3$ [d, $^2J(C,P) = 12.3$ Hz, C2], 135.0 [d, $^2J(C,P) = 14.6$ Hz, C6], 133.8 [d, $^4J(C,P) = 2.1$ Hz, C4], 131.6 [d, $^3J(C,P) = 13.1$ Hz, C3], 129.8 [d, $^3J(C,P) = 12.5$ Hz, C5], C1 not detected, 21.6 [s, Me]. $^{31}P\{^1H\}$ NMR (−50 °C): $\delta = 34.0$ [s, P(*m*-tol)$_3$]. IR (KBr): 2154 cm^{-1}, s, 2122 cm^{-1}, w, 2075 cm^{-1}, vw, ν(CN); 655 cm^{-1}, vs, ν(SbF). MS (FAB): $m/z = 1061$ (100%) $\{[(m\text{-tol})_3PAu]_2SCN\}^+$, 805 (34.5) $\{[(m\text{-tol})_3P]_2Au\}^+$, 501 (60.7) $[(m\text{-tol})_3PAu]^+$. Anal. Calc. for $C_{43}H_{42}Au_2F_6NP_2SSb$ (1296.50 g mol^{-1}): C, 39.8; H, 3.3; N, 1.1. Found: C, 40.5; H, 3.4; N, 1.1%.

4.12. (μ-Thiocyanato)-bis[(dimethylphenylphosphine)-gold] hexafluoroantimonate (**13**)

Following the procedure given for **10** using (Me_2Ph-P)AuCl (100 mg, 0.27 mmol), (Me_2PhP)AuSCN (106 mg, 0.27 mmol) and $AgSbF_6$ (120 mg, 0.35 mmol); Yield, 199 mg (76%), decomposes slowly at room temperature. ^{1}H NMR: $\delta = 7.53$–7.73 [m, 5H, Ph], 1.51 [s, 6H, Me]. $^{13}C\{^1H\}$ NMR: $\delta = 134.0$ [d, $^2J(C,P) = 13.1$ Hz, C2/6], 132.7 [d, $^4J(C,P) = 2.3$ Hz, C4], 130.7 [d, $^1J(C,P) = 63.0$ Hz, C1], 129.9 [d, $^3J(C,P) = 12.3$ Hz, C3/5], 15.5 [d, $^1J(C,P) = 40.7$ Hz, Me]. $^{31}P\{^1H\}$ NMR (−50 °C): $\delta = 5.38$ [s, PMe_2Ph]. IR (KBr): 2120 cm^{-1}, s, 2070 cm^{-1}, vw, ν(CN); 655 cm^{-1}, vs, ν(SbF).

4.13. (μ-Thiocyanato)-bis{[tri(^{i}propyl)phosphine]gold} hexafluoroantimonate (**14**)

Following the procedure given for **10** using [(^{i}Pro)$_3$P]AuCl (67 mg, 0.17 mmol), [(^{i}Pro)$_3$P]AuSCN (70 mg, 0.17 mmol) and $AgSbF_6$ (86 mg, 0.22 mmol); Yield, 107 mg (63%), decomposes slowly at room temperature. ^{1}H NMR: $\delta = 2.33$ [sept, $^3J(H,H) = 7.2$ Hz, 1H, CH], 1.32 [d, $^3J(H,H) = 7.2$ Hz, 6H, Me]. $^{31}P\{^1H\}$ NMR (−50 °C): $\delta = 69.6$ [s, P(^{i}Pro)$_3$]. IR (KBr): 2155 cm^{-1}, s, 2127 cm^{-1}, w, ν(CN); 656 cm^{-1}, vs, ν(SbF).

4.14. Crystal structure determination

The crystalline samples were placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Crystal data were collected using a Nonius DIP2020 system with monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation at −130 °C. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares calculations on F^2 (SHELXL-97). Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located and included into the refinement with isotropic contributions (**2**) or were placed in idealized positions and refined using a riding model with fixed isotropic contributions (**1**, **4**, **5** and **7**), respectively. Further information on crystal data, data collection and structure refinement are summarized in Table 2. Important interatomic distances and angles are shown in the corresponding figure captions.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 192917–192921 for compounds **1**, **2**, **4**, **5**, **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336-033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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