The Effect of Hard and Soft Donors on Structural Motifs in (Isocyanide)gold(I) Complexes

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In memoriam Luigi M. Venanzi

Treatment of the (isocyanide)gold(I) species LAuCl (L = ^{t}BuNC, 2,6-$Me_2C_6H_3NC$) with 4-mercaptobenzoic acid in the presence of NaOMe yields the complexes [Au(4-$SC_6H_4CO_2H$)L] in good yield. Reaction of LAuCl with 2-HSQn (Qn = quinoline) and 2-HSPy (Py = pyridine) under the same conditions provides the thiolato compounds [Au(2-SQn)L] and [Au(2-SPy)L], respectively. A structural investigation of the pyridylthiolato compound revealed chains of molecules with alternating medium and long Au–Au interactions. Treatment of this compound with HBF_4 results in the cationic species [Au(2-HSPy)(2,6-$Me_2C_6H_3NC$)]$^+$ as the BF_4^- salt. The same product is obtained on reaction of [AuCl(2,6-$Me_2C_6H_3NC$)] with AgOTf followed by HSPy. Treatment of the gold(I) halide compounds LAuCl (L = ^{t}BuNC, 2,6-$Me_2C_6H_3NC$) with potassium 1,3,4-thiadiazole-2,5-dithiolate (KSSSK) leads to the isolation of dinuclear thiolatogold complexes [$(AuL)_2$(SSS)]. These products go on to form insoluble polymers through loss of isocyanide on standing in solution. A single crystal of [{Au(^{t}BuNC)}$_2$(SSS)] was obtained and the subsequent structural analysis revealed one of the most complicated networks known based solely on aurophilic interactions. A good comparison to the 'soft' S-donation of the thiolato ligands was provided by the synthesis of a number of nitratogold(I)complexes with the anion bound through the 'hard' O-donor. Reaction of ^{i}PrNC and CyNC with Au(tht)Cl provided the complexes [AuCl(^{i}PrNC)] and [AuCl(CyNC)], respectively. These compounds were found to yield the respective nitrato species [Au(NO_3)^{i}PrNC)] and [(Au(NO_3)(CyNC)] on treatment with $AgNO_3$. The nitrato complexes yielded single crystals enabling a structural investigation to be carried out. While [Au(NO_3)(CyNC)] has a more conventional structure with dimers aligned into strings with alternating short and long aurophilic bonding, [Au(NO_3)(^{i}PrNC)] has a unique structure based on strings of alternating, corner-sharing Au_6 and Au_8 units with short Au–Au contacts in edge-sharing Au_3 triangles.

Introduction. – Isocyanidegold compounds have attracted increasing attention over the last decade due to their potential in a number of applications. Their use as MOCVD precursors for the deposition of Au films was first explored by *Puddephatt* and co-workers [1] in 1987. Since then, it has been shown that isocyanide gold alkynyls and halides have an important role to play in recent advances in the field of liquid crystal applications [2]. The observation that (isocyanide)gold(I) halides are able to form liquid crystalline phases is thought to arise from the presence of weak Au–Au interactions. Such interactions are facilitated by the low steric bulk of the isocyanide ligand which allows 'rod-like' molecules to be designed, as illustrated in the structures of examples such as [Au($C\equiv CSiMe_3$)(^{t}BuNC)] [3] and [$Au(MeNC)_2$]CF_3SO_3 [4]. Much research has been centered on the preparation and investigation of the properties of (acetylide)(isocyanide)gold complexes [5]. For example, complexes of the general formula [Au(4-$RC_6H_4C\equiv C$)(^{t}BuNC)] (R = NO_2, $C_6H_4NO_2$, *etc.*) [6] have been investigated in reference to their nonlinear optical properties. The possibility of combining the isocyanide and acetylide functionalities was elegantly demonstrated by *Puddephatt* with a series of acetylide (alkynyl)(isocyanoaryl)gold(I) complexes of the form $[Au(C{\equiv}C^tBu)(CNC_6H_4C{\equiv}CH)]$ [7].

The linear, sterically unencumbered nature of the isocyanide ligand leads to the observation of short Au–Au contacts in the solid state, as displayed in the cyano isocyanide example [AuCN(MeNC)] [8] as well as the complexes mentioned above. The related binuclear cyano species $[Au_2(CN)_2(dmb)]$ (dmb = 1,8-diisocyano-*p*-menthane) shows surprisingly short Au–Au interactions in addition to interesting luminescence behavior [9]. More recently, the isocyanide ligand has been employed to stabilize Au^I complexes with weakly coordinating anions such as $[AuNO_3(RNC)]$ (R = ^{t}Bu, 2,6-$Me_2C_6H_3$) [10]. The ^{t}Bu derivative was found to be an effective precursor for the deposition of Au on iron oxide in order to form a catalytically active surface for the low temperature oxidation of CO [11].

If one considers the enormously rich chemistry accessible from the $[Au(PR_3)]^+$ synthon, it is reasonable to expect that the analogous $[Au(RNC)]^+$ fragment should also lead to a similarly fascinating range of compounds. Due to the planar geometry of species such as $[Au(PhNC)]^+$, markedly different structures can be expected for these complexes. As mentioned above, in acetylide gold chemistry, the difference in steric requirements of the donor ligand (isocyanide *vs.* phosphine) has been exploited in the design of 'rod-like' molecules which are able to pack in different ways to those observed for phosphinogold complexes.

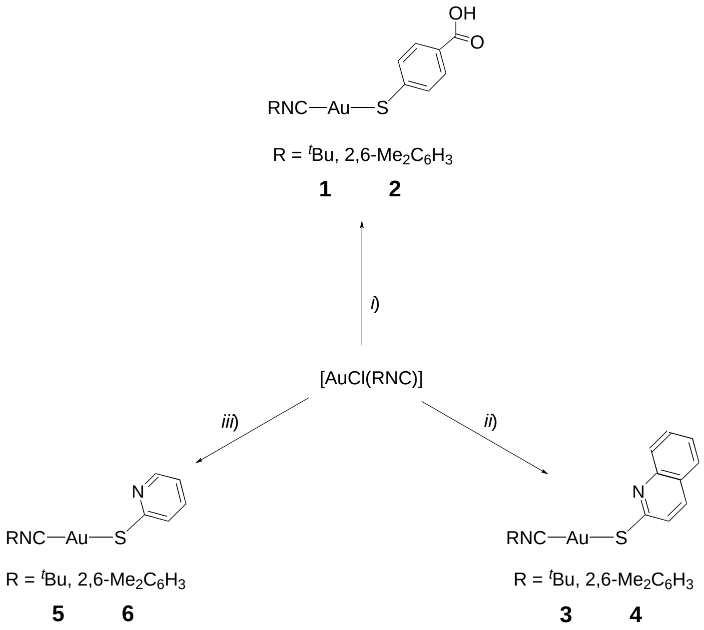
The application of gold thiolate species in fields as diverse as medicine [12], thin-film technology [13], and ceramics [14] has led to great interest in complexes of the general type $[Au(SR)(PR_3)]$ (R = alkyl, aryl) whether in mono- or polymetallic systems. As yet, relatively little effort has been expended in the field of (isocyanide)-gold(I) thiolate chemistry [15]. A recent report from *Bachman et al.* [16] concentrated on compounds of the form [Au(SPh)(RNC)] which were found to be unstable with respect to isocyanide loss and formation of a highly luminescent modification of $[Au(PhS)]_n$. This is in direct contrast to the behavior of the complexes $[Au(SR')(PR_3)]$ (R, R′ = alkyl, aryl) which show a greater stability [17].

Following recent work in this group on isocyanide thiocyanate complexes of Au^I [18], we have turned our attention to the coordination and structural chemistry of thiolates with the $[Au(RNC)]^+$ fragment. In a past report [15], we detailed the preparation and structural characterization of the thiosalicylate complexes $[Au(2\text{-}SC_6H_4CO_2H)(RNC)]$ (R = ^{t}Bu, 2,6-$Me_2C_6H_3$) which exhibited both Au–Au contacts and H-bonding interactions. These complexes are soluble in THF and show no tendency toward decomposition through loss of the isocyanide ligand. This is also in direct contrast to the observation by *Bachman et al.* [16] mentioned above. In order to probe the factors governing this differing reactivity, we decided to generate a number of novel (isocyanide)gold(I) thiolate examples by reaction of a range of thiols with (isocyanide)gold halide precursors. This report expands upon preliminary work detailed in a communication [19].

As mentioned above, recent work performed both in this group [10a] and by others [10b] has explored the area of gold nitrate chemistry. The (isocyanide)gold(I) nitrates included here serve to explore the effect of strongly electronegative substituents on the stability and structure of such species.

Results and Discussion. – *Thiolato Complexes.* Addition of one mole equivalent of 4-sulfanylbenzoic acid to the (isocyanide)gold(I) halide compounds [AuCl(RNC)] (R = ^{t}Bu, 2,6-Me$_2$C$_6$H$_3$) in the presence of NaOMe results in clean formation of the complexes [Au(4-SC$_6$H$_4$CO$_2$H)(RNC)] [R = ^{t}Bu, **1**; 2,6-Me$_2$C$_6$H$_3$, **2**] (*Scheme 1*). The presence of the isocyanide ligand was indicated by strong $\tilde{\nu}$(CN) absorptions at 2220 cm^{-1} (**1**) and 2207 cm^{-1} (**2**). Further confirmation was provided by the resonances in the ^{1}H-NMR spectrum. The H-atoms of the Me groups in **1** give rise to a sharp singlet at 1.58 ppm, whereas the isocyanide ligand in **2** displays resonances at 2.48 (*s*), 7.24 (*d*) and 7.38 (*t*) ppm with *J*(H,H) = 7.7 Hz. Similar patterns were found for all complexes discussed hereafter. In addition to these, resonances for the C$_6$H$_4$ unit were observed at 7.44, 7.65 (*AB*, *J*(H,H) = 8.4 Hz) and 10.96 (CO$_2$H) ppm. We have reported the preparation of the analogous complexes with carboxyl substitution at C(2). In view of recent work from these laboratories [15] demonstrating the radical structural changes brought about by changes in the substitution pattern of this ligand, it was unfortunate that no single crystals of **1** and **2** of suitable quality could be obtained.

Scheme 1

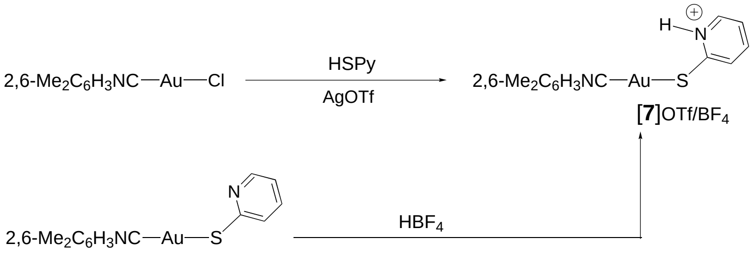


i) 2-HSC$_6$H$_4$CO$_2$H, NaOMe: *ii*) 2-HSQn, NaOMe. *iii*) 2-HSPy, NaOMe.

The ligands quinoline-2-thiol (2-HSQn) [20] and pyridine-2-thiol (2-HSPy) [21] have been shown to coordinate well to (phosphino)gold(I) fragments and such compounds with 2-HSPy have been investigated in the context of anti-tumor activity [22]. This made them attractive ligands with which to examine the coordination ability of the (isocyanide)gold(I) fragment. The planar, sterically undemanding nature of these isocyanides also makes their compounds suited to the formation of Au–Au contacts. The reactions of these ligands with the isocyanide complexes [AuCl(RNC)] (R = ^{t}Bu, 2,6-$Me_2C_6H_3$) proceed smoothly to provide [Au(2-SQn)(RNC)] (R = ^{t}Bu, **3**; 2,6-$Me_2C_6H_3$, **4**) and [Au(2-SPy)(RNC)] (R = ^{t}Bu, **5**; 2,6-$Me_2C_6H_3$, **6**) as pale yellow microcrystalline solids (*Scheme 1*). Characteristic spectroscopic data were observed for the isocyanide ligands. The thiolate groups gave rise to a number of resonances in the ^{1}H-NMR spectrum. For **5**, two *doublets* are observed at 7.54 and 7.74 ppm (J(H,H) = 8.7 Hz) for the H-atoms in the 3- and 6-position of the Py ring whereas the H–C(5) and H–C(4) protons give rise to *triplets* at 7.32 and 7.61 ppm (J(H,H) = 7.7 Hz). The resonances arising from the quinoline-2-thiolate ligand proved more difficult to assign individually.

Treatment of the complex [Au(2-SPy)(2,6-$Me_2C_6H_3NC$)] (**6**) with HBF_4 leads to the protonation of the Py group at the N-atom to provide [Au(2-HSPy)(2,6-$Me_2C_6H_3NC$)]OTf (**7**). The same product is accessible from the direct reaction of [AuCl(2,6-$Me_2C_6H_3NC$)] with pyridine-2-thiol in the presence of AgOTf (*Scheme 2*). This second route actually leads more cleanly and in higher yields to complex **7**. The ^{1}H-NMR spectrum of **7** reveals a new broad resonance for the protonated Py group at 12.50 ppm. A shift to lower frequency (2213 to 2217 cm^{-1}) is observed in the $\tilde{\nu}$(CN) absorption in the solid-state IR spectrum consistent with the assumption that the positive charge is delocalized throughout the molecule and not isolated on the Py N-atom. The presence of the TfO^{-} counterion is confirmed by microanalytical data.

Scheme 2. *Preparation of Complex* **7** *through Direct Reaction with Thiol or* via *Protonation*



[**7**]OTf/BF_4

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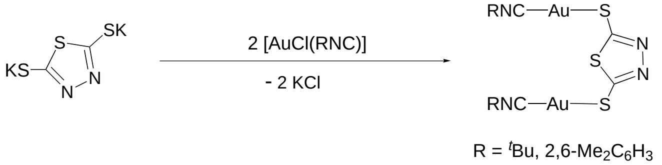
Treatment of a solution of 2 mol-equiv. of [AuCl(RNC)] (R = ^{t}Bu, 2,6-$Me_2C_6H_3$) in CH_2Cl_2 with one mole equivalent of potassium 1,3,4-thiadiazole-2,5-dithiolate, (KSSSK) in MeOH affords the colorless products [{Au(^{t}BuNC)}$_2$(SSS)] (R = ^{t}Bu, **8**; 2,6-$Me_2C_6H_3$, **9**) along with an insoluble, yellow material (*Scheme 3*). **8** and **9** are soluble in CH_2Cl_2 and $CHCl_3$, but insoluble in pentane. The ^{13}C-NMR spectra show the

Scheme 3. *Preparation of Bimetallic Examples* **8** *and* **9**



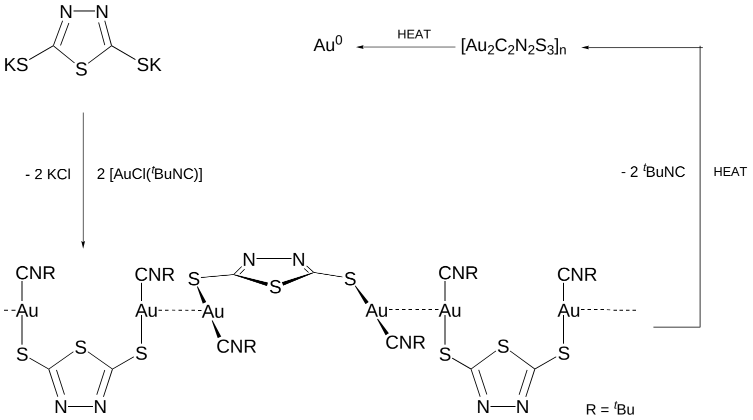
R = ^{t}Bu, 2,6-$Me_2C_6H_3$

8 **9**

expected resonances for the isocyanide ligand along with a *singlet* at 166.2 ppm attributable to the SSS unit. A strong $\tilde{\nu}$(CN) absorption for the isocyanide ligand in **8** is observed in the IR spectrum at 2232 cm^{-1}, whereas two bands (due to solid-state splitting effects) are seen at 2213 and 2207 cm^{-1} for **9**. In the FAB-MS, the parent ions M^+ are detected at $m/z = 710$ for **8** and $m/z = 804$ for **9**.

The compounds are stable when stored at low temperature, however, in contrast to the other results reported here, even microcrystalline powders of **8** and **9** show loss of ^{t}BuNC, a fact clearly indicated by the distinct isocyanide odor of the samples. Clear solutions in chlorocarbon solvents gradually form a yellow precipitate which cannot then be redissolved. Some of this yellow insoluble material was also observed in the initial stage of the preparation of the ^{t}BuNC complex. Microanalytical data^1) for the product indicate partial loss of the isocyanide ligand after several weeks at 20° leading to formation of the polymeric disulfide $[Au_2(SSS)]_n$. This process (shown in *Scheme 4*) can be accelerated by heating compound **8** under reflux in anaerobic conditions for 3 h in toluene or by heating the solid under vacuum. This is a similar degradation to that noticed recently by *Bachman et al.* [16]. Intensifying the thermal conditions further results in an even deposition of Au metal.

Scheme 4. *Polymerization and Decomposition Pathway for* **8**



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Nitrato Complexes. Direct reaction of the free isocyanide ligands with (tetrahydrothiophene)gold(I) chloride results in the isolation of the new isocyanide complexes [AuCl(^{i}PrNC)] (**10**) and [AuCl(CyNC)] (**11**) in good yield (*Scheme 5*). Strong absorptions in the solid state IR spectrum (2257 cm^{-1}, **10**; 2259 cm^{-1}, **11**) confirm coordination of the isocyanide ligands. The FAB-MS of complexes **10** and **11** failed to display molecular ions but did show abundant fragmentations for $[2M - Cl]^+$ ions. Such di(gold)chloronium cations bound by phosphino ligands have been shown to exist in the corresponding BF_4^-, ClO_4^-, and AsF_6^- salts [23].

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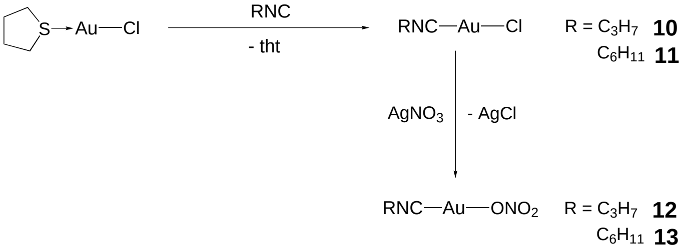
^{1}) Almost total elimination of the isocyanide ligand was observed. The conditions necessary to remove the remaining approx. 0.1 mole of ^{t}BuNC resulted in sample decomposition and the appearance of metallic Au. Anal. calc. for $[C_2Au_2N_2S_3]_n \cdot 0.1\ C_5H_9N$: C 5.45, H 0.16, N 5.34; found: C 5.62, H 0.20, N 5.27.

Scheme 5. *Preparation of Nitrato Complexes and Their Precursors*



Treatment of **10** and **11** with $AgNO_3$ in MeOH yields the complexes $[Au(NO_3)(^iPrNC)]$ (**12**) and $[Au(NO_3)(CyNC)]$ (**13**), respectively (*Scheme 5*). Solid state IR spectroscopic data confirm the retention of the isocyanide ligand (2263 cm^{-1}, **12**; 2267 cm^{-1}, **13**), the shift to higher frequency reflecting the electronic change brought about by the replacement of chloro for nitrato ligand. Microanalytical data confirm the empirical composition, as does the observation of molecular ions in the MS (CI) at $m/z = 328$ (**12**) and 369 (**13**). After even relatively short periods (few hours) in solution, deposition of elemental Au is observed. This is not noted for the precursors **10** and **11** and is in accordance with the weaker coordination ability of NO_3^- relative to that of Cl^-.

Together, the nitrato complexes **12** and **13** and the species detailed above permit a comparison of the effects related to the contrasting 'hard' (NO_3^-) and 'soft' (thiolate) donors to be drawn. Single crystals of both complexes **12** and **13** were obtained enabling this comparison to be extended to a structural investigation.

Structural Discussion. – Crystals of **6** (obtained from CH_2Cl_2/pentane) are triclinic, of space group $P\bar{1}$, with $Z = 2$ formula units in the unit cell. The asymmetric unit consists of one molecule with a slightly bent main axis comprising the atoms C(11)–N(1)–C(1)–Au(1)–S(1) (*Fig. 1*). The xylyl and the Py rings are virtually coplanar. The N-atom of the Py group (N(2)) is in a *Z*-shaped orientation regarding the Au(1)–S(1)–C(21)–N(2) conformation, *i.e.*, it is directed away from the Au-atom. Two molecules are arranged in pairs parallel and head-to-tail with the Au(1)–Au(1′) distance of 3.589(1) Å representing the shortest contact between the two molecules which are related by a center of inversion (*Fig. 2*). These dimers form strings of molecules with longer intermolecular Au(1)–Au(1″) contacts of 4.037(1) Å, in which all Au-atoms lie on a line with alternating distances and only slight puckering. No arene stacking is discernible either within each chain or between chains as shown in *Fig. 3*. This arrangement is not uncommon in the structural chemistry of (isocyanide)gold complexes. The literature has several examples of related organizational principles [4][10][16][18b]. It should be noted that the soft donor character of the thiolato ligand does not induce a significant shortening of the aurophilic contacts [24]. As with most other $[Au(RNC)]^+$ complexes, the Au–Au contacts remain around the upper limit of the range accepted for aurophilic bonding (2.9–3.6 Å). The contact between dimers is beyond the sum of the *Van der Waals radii*. Therefore metal–metal interactions should not be considered the determining structural factor in the shape of the string-like arrangement of molecules.

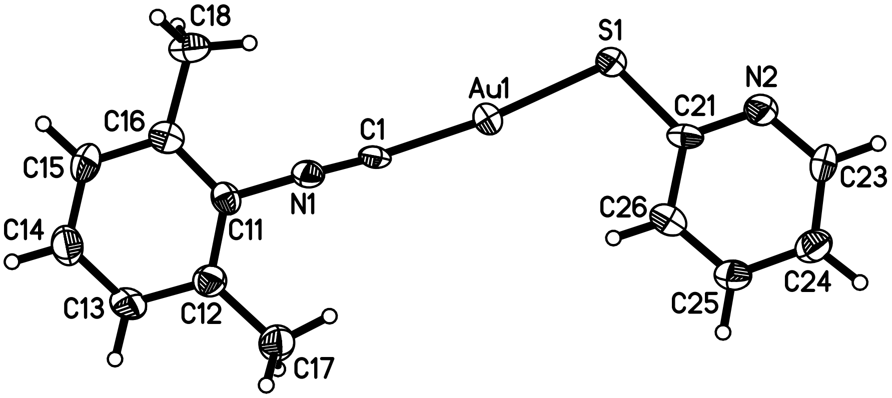


Fig. 1. *Molecular structure of* **6** (ORTEP, 50% probability ellipsoid). Selected bond lengths [Å] and angles [°]: Au(1)–C(1) 1.970(9), Au(1)–S(1) 2.267(2), C(1)–N(1) 1.13(1), N(1)–C(11) 1.41(1), S(1)–C(21) 1.740(8); C(1)–Au(1)–S(1) 174.0(2), Au(1)–S(1)–C(21) 108.9(3), N(1)–C(1)–Au(1) 175.5(8), C(1)–N(1)–C(11) 175.7(9).

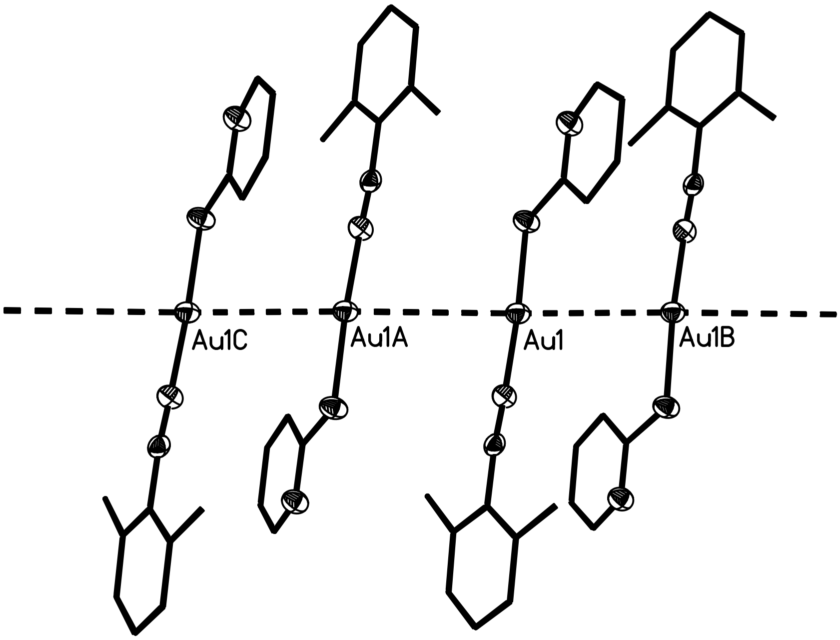


Fig. 2. *Chain of dimeric molecules in the structure of* **6** *with intra-dimer distance Au(1)–Au(1B) 3.589(1) Å and inter-dimer contacts Au(1)–Au(1A) 4.037(1) Å*

Crystals of **8** are monoclinic, of space group $P2_1/n$, with $Z = 12$ molecular (dinuclear) units in the unit cell. The asymmetric unit contains three independent molecules of similar geometry, one of which is shown in *Fig. 4* as a representative example. Both the molecular geometry and the packing (*Fig. 5*) have been described in

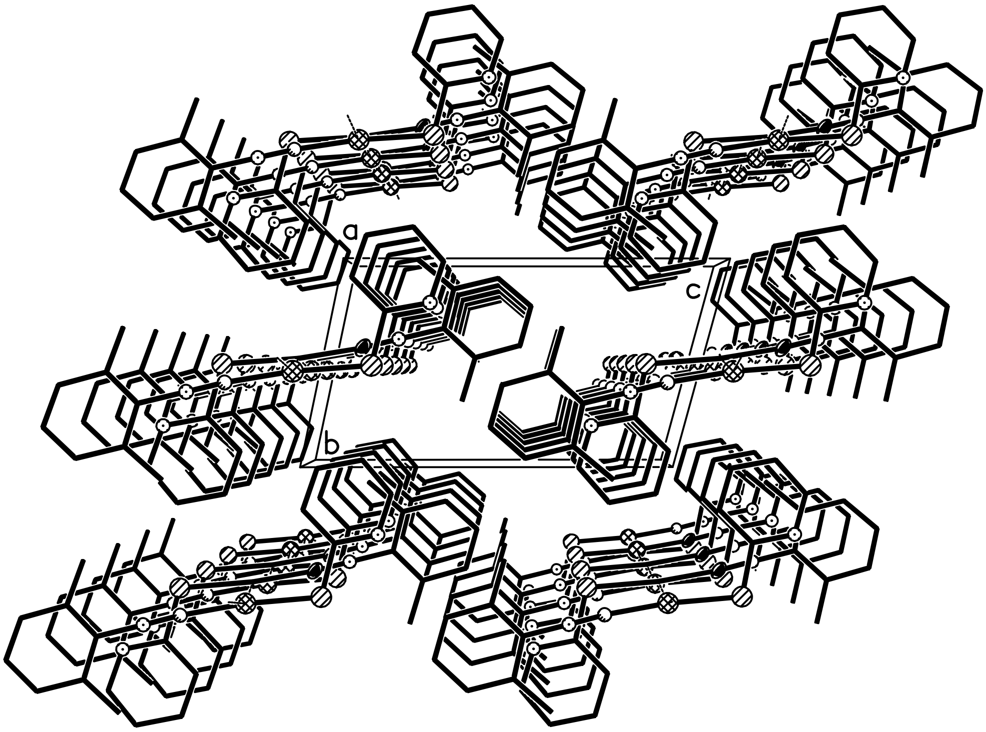


Fig. 3. *Projection along the chains of molecules in the crystal of* **6**. There is no arene stacking discernible.

a preliminary publication [19], and so the discussion will not be duplicated here. The structure, however, is included and will be referred to later as a reference for the three new structures. It is important to note that the structure of **8** displays double-strings of Au-atoms running parallel within the layers of the structure held together by relatively short Au–Au contacts (3.0447(3)–3.3476(4) Å). All Au–Au distances of neighboring metal atoms are thus well within the range for appreciable Au–Au interactions. The dinuclear character of the building blocks and the closely interwoven structure seem to support aurophilic bonding even for molecules with isocyanide ligands which are classified as strong σ-donors, but poor π-acceptors.

Crystals of [Au(NO_3)(CyNC)] (**13**) are monoclinic, space group $P2_1$/n, with $Z = 4$ formula units in the unit cell. The isocyanide ligand has the expected structure with a chair conformation for the six-membered ring. The individual complex molecules display a slightly bent five-atom axis C(11)–N(1)–C(1)–Au(1)–O(1) of standard bond lengths which are organized in centrosymmetrical dimers in which two monomers are coupled parallel and head-to-tail through a short Au–Au contact of 3.1839(4) Å (*Fig. 6*). The dimers are arranged in strings with long Au–Au distances of 3.9432(4) Å between them. The resulting chain of Au-atoms with alternating distances exhibits a zig-zag puckering. The NO_3^- groups are slightly twisted away from the center of the dimer to which they are attached. This brings one of the terminal O-atoms (O(2)) closer to a Au-atom of the neighboring dimer (at 3.4991(7) Å). Due to the long distance,

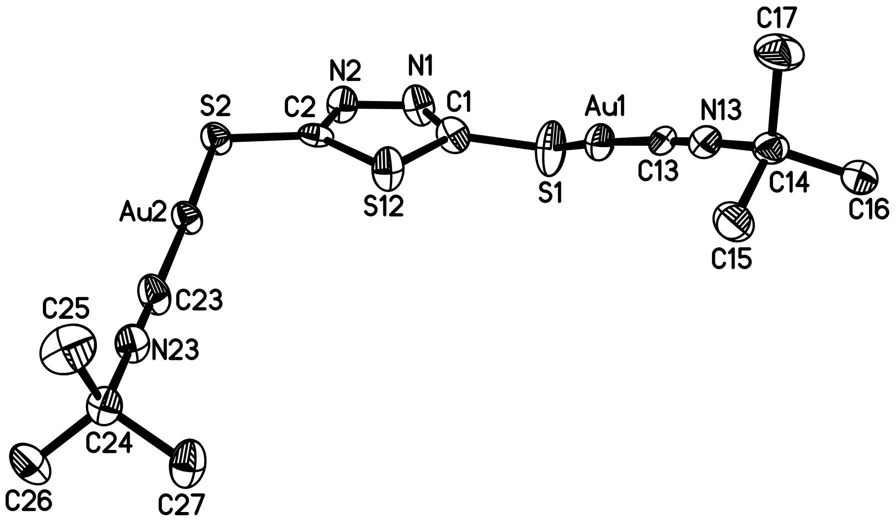


Fig. 4. *One of the three independent molecules in the structure of the dinuclear compound* **8**. The remaining two complexes have similar dimensions and conformations. Selected data were included in a preliminary communication [19].

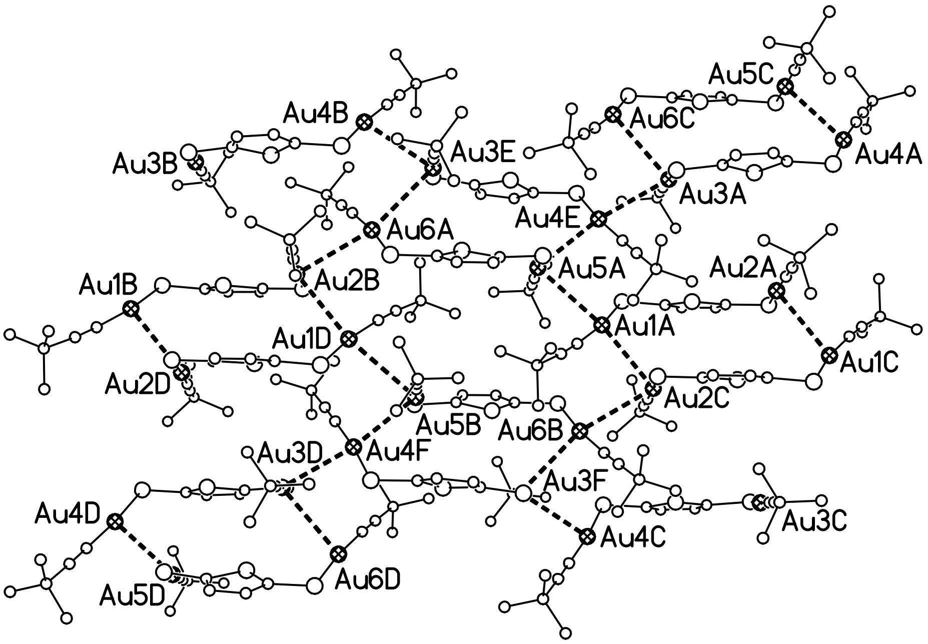


Fig. 5. *Arrangement of the dinuclear complex molecules of* **8** (*Fig. 4*) *in a layer structure*

however, the interactions will probably contribute very little to the lattice energy. The structure of **13** is of considerable interest because it shows that the introduction of an anionic ligand with a hard O donor atom causes the aurophilic bonds in the dimers to

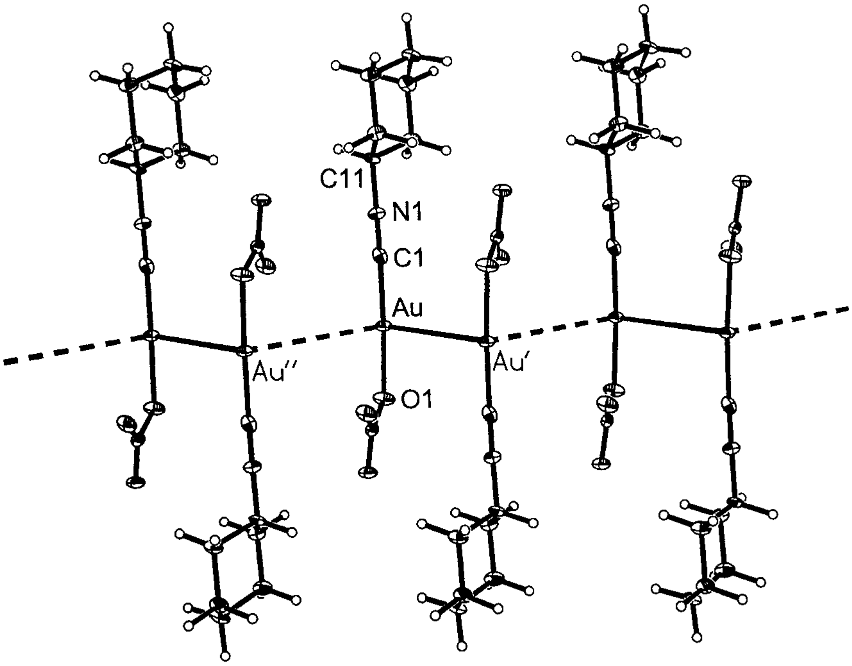


Fig. 6. *Chain of dimeric molecules in the structure of* **13** *with intra-dimer distances Au–Au′ 3.1839(4) Å and inter-dimer contacts Au–Au″ 3.9432(4) Å.* Selected bond lengths [Å] and angles [°]: Au–C(1) 1.874(7), Au–O(1) 2.005(5), N(1)–C(1) 1.111(9), N(1)–C(11) 1.410(7), N(2)–O(1) 1.243(8); C(1)–Au–O(1) 172.3(2), C(1)–N(1)–C(11) 178.0(7), N(2)–O(1)–Au 114.0(4), N(1)–C(1)–Au 177.7(6).

become shorter compared to those in **6**, where the soft donor atom of the thiolate anion leads to a much larger Au–Au separation. It should also be noted that there is no steric influence imposed by the Cy groups which appear to be accommodated strain-free at the periphery of the chains (*Fig. 6*).

Crystals of $[Au(NO_3)(^{i}PrNC)]$ (**12**) are triclinic, of space group $P\bar{1}$, with $Z=12$ formula units in the unit cell. The asymmetric unit contains six independent molecules with similar dimensions, one of which is shown in *Fig. 7.* The axes C–N–C–Au–O are almost perfectly linear with the usual bond lengths. These molecules are assembled into exceedingly complex chains, in which the Au-atoms form two different types of planar units sharing corners: In a suitable projection (*Fig. 8*), centrosymmetric units of six Au-atoms are discernible in which two atom triples Au(1)–Au(2)–Au(3) sit next to each other (head-to-tail, Au(1)–Au(2)–Au(3) 173.53(1)°) to form a set of four edge-sharing triangles. This set of Au-atoms is found to share its terminal Au-atoms Au(3) with another set of eight Au-atoms with two chains Au(3)–Au(4)–Au(5)–Au(6) also paired head-to-tail to form six edge-sharing Au triangles. The angles Au(3)–Au(4)–Au(5) (177.97(1)°) and Au(4)–Au(5)–Au(6) (175.1(1)°) are both close to linear. The 'raft-like' Au_6 and Au_8 platforms are virtually planar as shown in the three projections provided in *Figs. 8a–f.*

The edges of all Au triangles are well within the range of aurophilic bonding; between 3.0578(5) Å for Au(5)–Au(5′) and 3.4672(4) Å for Au(5)–Au(6). The atoms

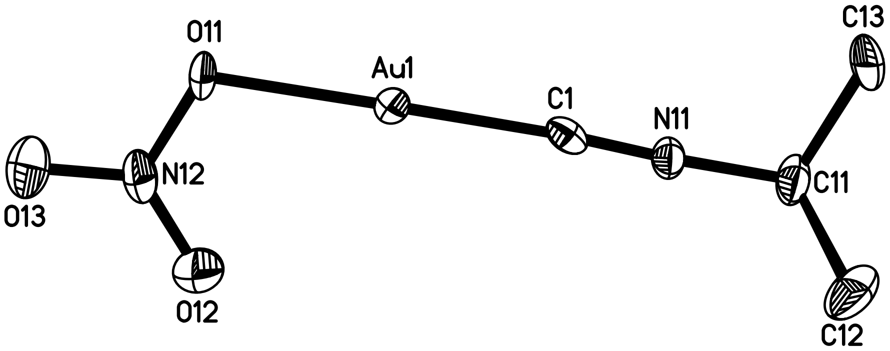


Fig. 7. *Molecular structure of one of the six independent molecules of* **12** (ORTEP, 50% probability ellipsoids, H-atoms omitted). Selected bond lengths [Å] and angles [°]: Au(1)−C(1) 1.92(1), Au(1)−O(11) 2.048(6), C(1)−N(11) 1.12(1), N(11)−C(11) 1.49(1); O(11)−Au(1)−C(1) 174.1(3), Au(1)−C(1)−N(11) 176.6(9), C(1)−N(11)−C(11) 175(1), Au(1)−O(11)−N(12) 114.9(4).

Au(1) and Au(6) maintain three close Au contacts, while Au(2), Au(3), Au(4), and Au(5) entertain their four closest Au neighbors.

The molecular axes of neighboring [Au(NO_3)(^{i}PrNC)] complexes in a given unit are roughly parallel but, through the tilting of the units against each other, the ligands point in different directions. Because of this variation in orientation of the isocyanide and NO_3^- groups, the Au core of one chain is shielded on all sides and well separated from neighboring strings (*Fig. 9*). The lattice contains no solvent molecules.

The complicated structure of the ^{i}PrNC complex **12** comes as a surprise after the relatively simple pattern found for the CyNC complex **13**, and even more so since both complexes have the same NO_3^- ligand. It should be noted that if one were to 'trim' the C-atoms C(3)−C(5) of the Cy substituent, one would, in effect, have an ^{i}Pr group. The steric requirements of an ^{i}Pr group in the coordination environment of the Au-atoms are therefore comparable to that of the Cy group. The changes in steric bulk should have a major effect only in the periphery of the molecular chains, and yet the packing of the molecules **12** and **13** is entirely different. It appears that the efficient packing of the molecular chains (*i.e.*, the space-filling accommodation of the ^{i}Pr/Cy and NO_3^- groups) is perhaps more significant than commonly expected. The pattern of the weak aurophilic interactions is therefore influenced significantly by these packing forces.

Conclusion. – The structures of a number of new (isocyanide)gold(I) complexes with both hard and soft co-ligands have been determined. The range of supramolecular structural motifs encountered demonstrates the fascinating and unpredictable nature of structures determined by aurophilic interactions. Two of the structures reported here (**8** and **12**) can be considered among the most complicated observed for molecules bound exclusively through intermetallic contacts. The (isocyanide)gold thiolate and nitrate compounds demonstrate the versatility of the $(AuRNC)^+$ fragment which, compared to the ubiquitous $(AuPR_3)^+$ species, has been much neglected in the field of (isocyanide)gold(I) chemistry.

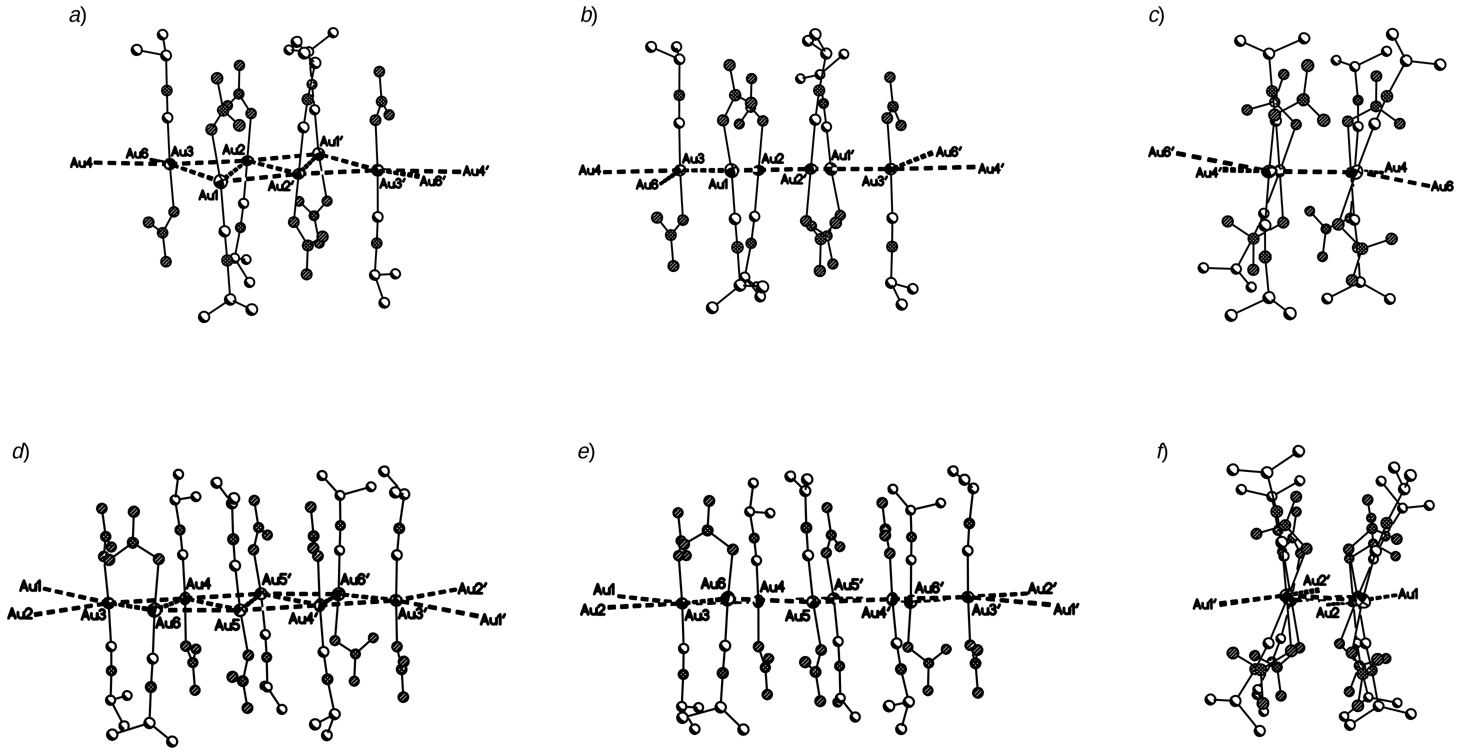


Fig. 8. a) *Perspective view of the* Au_6 *unit within one of the chains in the structure of* **12**. b) *and* c) *Projections of the same unit parallel to the layer of the Au-atoms showing the planarity of the unit.* d) *Perspective view of the* Au_8 *unit in one of the chains of* **12**. e) *and* f) *Projections of the same unit parallel to the layer of Au-atoms showing the planarity of the unit*. The Au_6 and Au_8 units share corners (Au(3)). The isocyanide ligands are aligned head to tail and project away from the Au layers with differing angles.

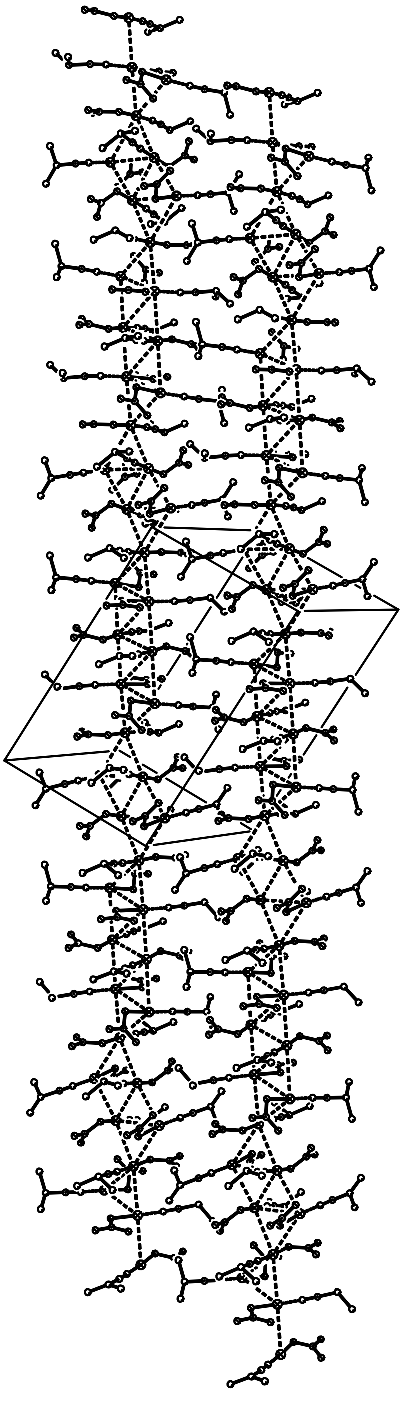


Fig. 9. *Projection of the chains present in the unit-cell of crystals of* **12**

Experimental Part

General. The experiments were carried out routinely in air. Potassium 1,3,4-thiadiazole-2,5-dithiolate (KSSSK), 4-sulfanylbenzoic acid, pyridine-2-thiol and quinoline-2-thiol were obtained commercially. The compounds [AuCl(^{t}BuNC)] [25], [AuCl(2,6-Me$_2$C$_6$H$_3$NC)] [26], Au(tht)Cl (tht = tetrahydrothiophene) [26], isopropylisocyanide [27], and cyclohexylisocyanide [27] were prepared following literature procedures. IR Spectra: *Perkin-Elmer 1600 Series* FT-IR Spectrometer; in KBr/Nujol; in cm^{-1}. NMR: *JEOL GX-400* spectrometer using deuterated solvents with the usual standards at 25°; δ in ppm, J(H,H) in Hz. MS: *Varian MAT311A* instrument (FAB, 4-nitrophenylmethanol); m/z (rel. %).

[Au(4-SC$_6$H$_4$CO$_2$H)(^{t}BuNC)] (**1**). A soln. of [AuCl(^{t}BuNC)] (120 mg, 0.38 mmol) in CH$_2$Cl$_2$ (10 ml) was treated dropwise with a soln. of 4-sulfanylbenzoic acid (60 mg, 0.39 mmol) and NaOMe (23 mg, 0.43 mmol) in MeOH (5 ml). The mixture was stirred for 1 h, and solvent was removed. The crude product was triturated in H$_2$O (20 ml) to remove NaCl and excess NaOMe. A colorless product was collected, washed with H$_2$O (10 ml) and pentane (10 ml), and dried. Yield: 100 mg (61%). IR: 2220 ($\tilde{\nu}$(CN)). ^{1}H-NMR ((D$_8$)THF): 1.58 (*s*, 3 Me); 7.44, 7.65 (*AB*, $J = 8.4$, C$_6$H$_4$); 10.96 (br. *s*, CO$_2$H). FAB-MS: 714 (33, [M + ^{t}BuNC]$^+$), 434 (100, M^+), 377 (100, [M – ^{t}Bu]$^+$), 363 (30, [Au(^{t}BuNC)$_2$]$^+$). Anal. calc. for C$_{12}$H$_{14}$AuNO$_2$S: C 33.27, H 3.26, N 3.23; found: C 32.75, H 3.00, N 2.77.

[Au(4-SC$_6$H$_4$CO$_2$H)(2,6-Me$_2$C$_6$H$_3$NC)] (**2**). As for **1**, with [AuCl(2,6-Me$_2$C$_6$H$_3$NC)] (90 mg, 0.25 mmol), 4-sulfanylbenzoic acid (38 mg, 0.25 mmol), and NaOMe (15 mg, 0.28 mmol). Yield: 82 mg (69%). IR: 2207 ($\tilde{\nu}$(CN)). ^{1}H-NMR ((D$_8$)THF): 2.48 (*s*, 2 Me); 7.24 (*d*, $J = 7.7$, H–C(3), H–C(5) of C$_6$H$_3$); 7.38 (*t*, $J = 7.7$, H–C(4) of C$_6$H$_3$); 7.49, 7.68 (*AB*, $J = 8.4$, C$_6$H$_4$), 10.90 (br. *s*, CO$_2$H). FAB-MS: 482 (6, M^+). Anal. calc. for C$_{16}$H$_{14}$AuNO$_2$S: C 39.93, H 2.93, N 2.91; found: C 39.44, H 2.88, N 2.84.

[Au(2-SQn)(^{t}BuNC)] (**3**). A soln. of [AuCl(^{t}BuNC)] (50 mg, 0.16 mmol) in CH$_2$Cl$_2$ (10 ml) was treated dropwise with a soln. of quinoline-2-thiol (26 mg, 0.16 mmol) and NaOMe (10 mg, 0.19 mmol) in MeOH (5 ml). The mixture was stirred for 1 h, and solvent was removed. The crude solid was dissolved in CH$_2$Cl$_2$ (10 ml) and filtered through diatomaceous earth. Et$_2$O (15 ml) was added to the filtrate to precipitate a pale yellow product which was washed with Et$_2$O (10 ml) and dried. The product was found to become only sparingly soluble in chlorinated solvents after precipitation from CH$_2$Cl$_2$/pentane. Yield: 43 mg (62%). IR: 2222 ($\tilde{\nu}$(CN)). ^{1}H-NMR (CD$_2$Cl$_2$): 1.56 (*s*, 3 Me); 7.33 (*t*, $J = 8.0$, 1 H of SQn); 7.53 (*d*, $J = 8.0$, 1 H of SQn); 7.63 (*d*, $J = 8.5$, 1 H of SQn); 7.75 (*d*, $J = 8.5$, 1 H of SQn). FAB-MS: 720 (28, [2M – SQn]$^+$), 441 (44, M^+), 385 (100, [M – ^{t}Bu]$^+$). Anal. calc. for C$_{14}$H$_{15}$AuN$_2$S: C 38.19, H 3.43, N 6.36; found: C 38.70, H 3.50, N 6.21.

[Au(2-SQn)(2,6-Me$_2$C$_6$H$_3$NC)] (**4**). As for **3**, with [AuCl(2,6-Me$_2$C$_6$H$_3$NC)] (50 mg, 0.14 mmol), quinoline-2-thiol (22 mg, 0.14 mmol) and NaOMe (8 mg, 0.15 mmol). Yield: 48 mg (72%). IR: 2205 ($\tilde{\nu}$(CN)). ^{1}H-NMR (CD$_2$Cl$_2$): 2.46 (*s*, 2 Me); 7.15 (*d*, $J = 7.4$, H–C(3), H–C(5) of Ph); 7.38 (*t*, $J = 7.4$, 1 H of SQn); 7.40 (*t*, $J = 7.4$, H–C(4) of Ph); 7.54 (*d*, $J = 8.7$, 1 H of SQn); 7.59 (*d*, $J = 7.5$, 1 H of SQn); 7.66 (*d*, $J = 7.5$, 1 H of SQn); 7.82 (*d*, $J = 8.7$, 1 H of SQn). FAB-MS: 816 (33, [2M – SQn]$^+$), 490 (100, M^+), 358 (60, [M – C$_9$H$_9$N]$^+$). Anal. calc. for C$_{18}$H$_{15}$AuN$_2$S: C 44.27, H 3.10, N 5.74; found: C 44.50, H 3.23, N 6.01.

[Au(2-SPy)(^{t}BuNC)] (**5**). A soln. of [AuCl(^{t}BuNC)] (50 mg, 0.16 mmol) in CH$_2$Cl$_2$ (10 ml) was treated dropwise with a soln. of pyridine-2-thiol (18 mg, 0.16 mmol) and NaOMe (10 mg, 0.19 mmol) in MeOH (5 ml). After stirring for 1 h, solvent was removed and the crude solid dissolved in CH$_2$Cl$_2$ (10 ml) and filtered through diatomaceous earth. Et$_2$O (15 ml) was added to the filtrate to precipitate a colorless product which was washed with Et$_2$O (10 ml) and dried. The product was found to become only sparingly soluble in chlorinated solvents after precipitation from CH$_2$Cl$_2$/pentane. Yield: 31 mg (50%). IR: 2247, 2228 ($\tilde{\nu}$(CN)). ^{1}H-NMR (CD$_2$Cl$_2$): 1.56 (*s*, 2 Me); 7.32 (*t*, $J = 7.7$, H–C(5) of Py); 7.54 (*d*, $J = 8.7$, H–C(3) of Py); 7.61 (*t*, $J = 7.7$, H–C(4) of Py); 7.74 (*d*, $J = 8.7$, H–C(6) of Py). FAB-MS: 391 (20, M^+), 335 (16, [M – ^{t}Bu]$^+$), 308 (8, [M – ^{t}BuNC]$^+$). Anal. calc. for C$_{10}$H$_{13}$AuN$_2$S: C 29.14, H 3.26, N 6.47; found: C 28.74, H 3.00, N 6.74.

[Au(2-SPy)(2,6-Me$_2$C$_6$H$_3$NC)] (**6**). As for **5**, with [AuCl(2,6-Me$_2$C$_6$H$_3$NC)] (50 mg, 0.14 mmol), pyridine-2-thiol (15 mg, 0.14 mmol) and NaOMe (8 mg, 0.15 mmol). Yield: 52 mg (86%). IR: 2213 ($\tilde{\nu}$(CN)). ^{1}H-NMR (CD$_2$Cl$_2$): 2.43 (*s*, 2 Me); 6.91 (*t*, $J = 7.1$, H–C(5) of Py); 7.15 (*d*, $J = 7.6$, H–C(4), H–C(5) of Ph); 7.32 (*t*, $J = 7.6$, H–C(4) of Ph); 7.41 (*d*, $J = 6.0$, H–C(3) of Py); 7.44 (*t*, $J = 7.1$, H–C(4) of Py). FAB-MS: 766 (20, [2M – SPy]$^+$), 438 (100, M^+), 328 (9, [M – SPy]$^+$), 308 (28, [M – CNX]$^+$). Anal. calc. for C$_{14}$H$_{13}$AuN$_2$S · 1.5 CH$_2$Cl$_2$: C 36.23, H 2.94, N 5.83; found: C 36.18, H 3.18, N 5.84.

[Au(2-HSPy)(2,6-Me$_2$C$_6$H$_3$NC)]OTf (**7**). a) (50 mg, 0.19 mmol) was added to a stirred soln. of [AuCl(2,6-Me$_2$C$_6$H$_3$NC)] (70 mg, 0.19 mmol) in THF (20 ml) at 0°. After 5 min stirring, during which the formation of Au colloid was observed, pyridine-2-thiol (21 mg, 0.19 mmol) was added and the mixture stirred for a further 25 min. Solvent was removed and the crude product was dissolved in CH$_2$Cl$_2$ (10 ml) and filtered through

diatomaceous earth. Et_2O (15 ml) was added to the filtrate to precipitate a pale yellow product which was washed with Et_2O (10 ml) and dried. Yield: 81 mg (72%).

b) A soln. of HBF_4 in Et_2O (4 drops) was added to a stirred soln. of [Au(2-SPy)(2,6-$Me_2C_6H_3$NC)] (50 mg, 0.114 mmol) in CH_2Cl_2/MeOH (20 ml, 1:1). After stirring for 20 min, solvent was removed, and the product extracted into CH_2Cl_2 (2 × 10 ml). The volume of the extracts was reduced to *ca.* 5 ml and Et_2O (20 ml) added to precipitate the pale yellow product. Yield: 38 mg (65%). IR: 2217 ($\tilde{\nu}$(CN)). ^{1}H-NMR (CD_2Cl_2): 2.50 (*s*, 2 Me); 7.21 (*d*, *J* = 7.7, H–C(3), H–C(5) of Ph); 7.31 (*t*, *J* = 6.9, H–C(5) of Py); 7.38 (*t*, *J* = 7.7, H–C(4) of Ph); 7.78 (*d*, *J* = 7.4, H–C(3) of Py); 7.86 (*t*, *J* = 6.9, H–C(4) of Py); 8.42 (*d*, *J* = 7.4, H–C(6) of Py); 12.50 (br., NH). FAB-MS: 765 (2, [2*M* – SPy]$^+$), 439 (100, M^+), 328 (4, [*M* – SPy]$^+$). Anal. calc. for $C_{15}H_{14}AuF_3N_2O_3S_2$: C 30.62, H 2.40, N 4.76; found: C 30.61, H 2.22, N 4.56.

[{Au(^{t}BuNC)}$_2$(SSS)] (**8**). A soln. of KSSSK (36 mg, 0.16 mmol) in MeOH (5 ml) was added dropwise to a stirred soln. of [AuCl(^{t}BuNC)] (100 mg, 0.32 mmol) in CH_2Cl_2 (15 ml). After stirring for 2 h, a fine yellow precipitate was present. Solvent was removed, and the crude product dissolved in CH_2Cl_2 (20 ml) and filtered through diatomaceous earth to remove the yellow solid. After concentration of the soln. to *ca.* 10 ml, pentane (20 ml) was carefully added to precipitate a colorless solid. This was washed with pentane (20 ml) and dried. Yield: 79 mg (70%). IR: 2232 ($\tilde{\nu}$(CN)). ^{1}H-NMR ($CDCl_3$): 1.58 (*s*, Me). ^{13}C-NMR (CD_2Cl_2): 166.2 (*s*, $C_2N_2S_3$); 140.7 (br. *s*, ^{t}BuN*C*); 59.0 (*s*, *C*Me_3); 29.5 (*s*, Me). FAB-MS: 710 (6, M^+). Anal. calc. for $C_{12}H_{18}Au_2N_4S_3$: C 20.34, H 2.56, N 7.91; found: C 20.15, H 2.37, N 7.84.

[{Au(2,6-$Me_2C_6H_3$NC)}$_2$(SSS)] (**9**). A soln. of KSSSK (31 mg, 0.14 mmol) in MeOH (5 ml) was added dropwise to a stirred soln. of [AuCl(2,6-$Me_2C_6H_3$NC)] (100 mg, 0.28 mmol) in CH_2Cl_2 (15 ml). After stirring for 2 h, a substantial amount of a fine, yellow precipitate was present. Solvent was removed and the crude product dissolved in CH_2Cl_2 (20 ml) and filtered through diatomaceous earth to remove the yellow solid. After concentration of the soln. to *ca.* 10 ml, pentane (20 ml) was carefully added to precipitate a colorless solid. This was washed with pentane (20 ml) and dried. Yield: 43 mg (39%). IR: 2213, 2207 ($\tilde{\nu}$(CN)). ^{1}H-NMR ((D_8)THF): 2.44 (*s*, 2 Me); 7.17 (*d*, *J* = 7.5, H–C(3), H–C(5) of Ph); 7.34 (*t*, *J* = 7.6, H–C(4) of Ph). FAB-MS: 804 (5, M^+). Anal. calc. for $C_{20}H_{18}Au_2N_4S_3$: C 29.86, H 2.26, N 6.96; found: C 29.43, H 2.38, N 7.21.

[AuCl(^{i}PrNC)] (**10**). A suspension of Au(tht)Cl (2.20 g, 6.86 mmol) in CH_2Cl_2 (20 ml) was treated with ^{i}PrNC (1 ml, 10.10 mmol) to give a clear soln. After stirring for 1 h, solvent and other volatiles were removed under vacuum. The residue was redissolved in 5 ml of CH_2Cl_2. Colorless crystals of the product were obtained by the diffusion of pentane vapor into the soln. in a closed system at –20°. Yield: 1.76 g (85%). IR: 2257 ($\tilde{\nu}$(CN)). ^{1}H-NMR ($CDCl_3$): 4.10 (*sept.*, *J* = 7.0, C*H*Me_2), 1.50 (*d*, *J* = 7.0, 2 Me). ^{13}C-NMR ($CDCl_3$): 132.8 (br. *s*, *C*N); 49.5 (*s*, *C*HMe_2); 22.2 (*s*, Me). FAB-MS: 799 (3, [3*M* – Cl]$^+$), 567 (100, [2*M* – Cl]$^+$), 335 (7, [Au(^{i}PrNC)$_2$]$^+$), 266 (4, [*M* – Cl]$^+$). Anal. calc. for C_4H_7AuClN: C 15.92, H 2.34, N 4.65; found: C 15.77, H 2.49, N 4.64.

[AuCl(CyNC)] (**11**). As for **10**, with Au(tht)Cl (2.00 g, 6.24 mmol) and CyNC (1 ml, 8.00 mmol) in 20 ml of CH_2Cl_2. Yield: 1.85 g (87%). Colorless microcrystals. IR: 2259 ($\tilde{\nu}$(CN)). ^{1}H-NMR ($CDCl_3$): 3.88, 1.98, 1.76, 1.43, (4*m*, 1:2:4:4 H of Cy). ^{13}C-NMR ($CDCl_3$): 55.0, 31.7, 24.5, 22.5 (4*s*, Cy) (CN resonance not observed). FAB-MS: 647 (70, [2*M* – Cl]$^+$), 415 (22, [Au(CyNC)$_2$]$^+$). Anal. calc. for $C_7H_{11}AuClN$: C 24.61, H 3.25, N 4.10; found: C 24.61, H 3.17, N 4.06.

[Au(NO_3)(^{i}PrNC)] (**12**). (Isopropylisocyanide)gold(I) chloride (**10**; 1.00 g, 3.32 mmol) was dissolved in CH_2Cl_2 (30 ml) and added slowly to a stirred soln. of $AgNO_3$ (0.70 g, 4.12 mmol) in MeOH (30 ml) at –78°. After 1 h, the solvent was removed under vacuum, and the residue dissolved in CH_2Cl_2 (10 ml). Crystallization as for **10**. Yield: 0.60 g (55%). IR: 2263 ($\tilde{\nu}$(CN)). ^{1}H-NMR ($CDCl_3$): 4.16 (*sept.*, *J* = 7.0, C*H*Me_2); 1.49 (*d*, *J* = 7.0, 2 Me). ^{13}C-NMR ($CDCl_3$): 122.2 (br. *s*, CN); 50.2 (*s*, *C*HMe_2); 21.9 (*s*, Me). CI-MS: 328 (23, M^+). Anal. calc. for $C_4H_7AuN_2O_3$: C 14.64, H 2.15, N 8.54; found: C 14.63, H 2.04, N 8.60.

[Au(NO_3)(CyNC)] (**13**). As for **12**, with (cyclohexylisocyanide)gold(I) chloride (**11**; 0.50 g, 1.46 mmol) and $AgNO_3$ (0.30 g, 1.77 mmol) in CH_2Cl_2/MeOH (10 ml : 15 ml). Yield: 0.33 g (61%). Colorless crystals. IR: 2267 ($\tilde{\nu}$(CN)). ^{1}H-NMR ($CDCl_3$): 3.96, 1.95, 1.70, 1.36 (4*m*, 1:2:4:4 H of Cy). ^{13}C-NMR ($CDCl_3$): 122.2 (br. *s*, CN); 55.7, 31.2, 24.3, 22.6 (4*s*, Cy). CI-MS: 369 (2M^+). Anal. calc. for $C_7H_{11}AuN_2O_3$: C 22.84, H 3.01, N 7.61; found: C 23.23, H 2.90, N 7.66.

Crystallography. Specimens of suitable quality and size 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 MoK_α radiation. Intensity data for all compounds were corrected for absorption effects (DELABS). 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 thermal motion was treated anisotropically for all non-H-atoms. All H-atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions ($U_{\text{iso(fix)}} = 1.5 \times U_{\text{eq}}$ of the attached C-atom). Further information on crystal data, data collection and structure refinement are summarized in the *Table*[2]). Important interatomic distances and angles are given in the corresponding figure captions.

Table 1. *Crystal Data, Data Collection, and Structure Refinement for* **6**, **8**, **12** *and* **13**.

	[Au(SPy)(2,6-$Me_2C_6H_3NC$)] (**6**)	[{Au(^tBuNC)}$_2$(SSS)] (**8**)	[Au(NO_3)(^iPrNC)] (**12**)	[Au(NO_3)(CyNC)] (**13**)
Crystal data				
Formula	$C_{14}H_{13}AuN_2S$	$C_{12}H_{18}Au_2N_4S_3$	$C_4H_7AuN_2O_3$	$C_7H_{11}AuN_2O_3$
M_r	438.29	708.42	328.08	368.14
Crystal system	triclinic	monoclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a [Å]	7.5855(3)	13.9440(1)	10.9194(1)	6.1624(1)
b [Å]	7.9758(3)	18.4157(2)	12.3663(1)	23.4436(4)
c [Å]	12.6376(7)	21.9061(2)	18.0092(3)	6.2240(1)
α [°]	101.812(2)	90	77.739(1)	90
β [°]	90.751(3)	95.244(1)	85.929(1)	101.581(1)
γ [°]	116.418(3)	90	71.342(1)	90
V [Å^3]	665.5(1)	5601.7(1)	2251.5(1)	880.9(1)
ρ_{calc} [g cm^{-3}]	2.187	2.520	2.904	2.776
Z	2	12	12	4
$F(000)$	412	3888	1776	680
μ(MoK_α) [cm^{-1}]	111.92	160.29	195.54	166.68
Data collection				
T [°]	-130	-130	-130	-130
Measured reflections	25633	161073	77449	37734
Unique reflections	2370 [$R_{int} = 0.040$)	12224 [$R_{int} = 0.060$]	9135 [$R_{int} = 0.048$]	2063 [$R_{int} = 0.063$]
Refinement				
Refined parameters	163	568	541	118
Final R values [$I = 2\sigma(I)$]				
$R1$	0.0490	0.0357	0.0333	0.0396
$wR2$	0.1464	0.0801	0.0824	0.1089
Weighting scheme[a])	$a = 0.1165$	$a = 0.00$	$a = 0.00$	$a = 0.0654$
	$b = 0.81$	$b = 34.60$	$b = 7.55$	$b = 5.50$

[a]) $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$; $p = (F_o^2 + 2F_c^2)/3$.

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[2]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC 172317–172320. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44(1223)336 033; e-mail: deposit@ccdc.cam.ac.uk).

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