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Supramolecular chemistry of gold(I) thiocyanate complexes with thiophene, phosphine and isocyanide ligands, and the structure of 2,6-dimethylphenyl isocyanide

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The reaction of equivalent quantities of (L)AuCl (L = tetrahydrothiophene, trimethylphosphine, 2,6-xylyl isocyanide or mesityl isocyanide) and KSCN in CH_2Cl_2–water gave (L)Au(SCN) in excellent yield. The products were formed through Cl ⟷ (SCN) anion exchange in the two-phase systems. Crystals of (THT)Au(SCN) contain short interion Au · · · Au contacts (3.006 Å) within chain polymers of alternating cations $[Au(THT)_2]^+$ and anions $[(NCS)_2Au]^-$. The crystal structure of $(Me_3P)Au(SCN)$ exhibits dimers based on short Au · · · Au contacts of 3.099 Å. The dimers appear to aggregate further by long Au · · · S contacts giving a tetrameric motif. Molecules of (2,6-$Me_2C_6H_3NC$)-Au(SCN) crystallise as flat, centrosymmetric dimers with long intermolecular Au · · · Au and Au · · · S contacts. Although the general aurophilic motif of (2,4,6-$Me_3C_6H_2NC$)Au(SCN) is similar to (2,6-$Me_3C_6H_3NC$)Au(SCN), its structure has two different dimers formed from similar monomers. The crystal structure of 2,6-$Me_2C_6H_3NC$ was also characterised and (consistent with bonding theory of metal isocyanides) exhibited a C≡N bond which is slightly longer than in the gold(I) complex.

Introduction

Current research in Crystal Engineering is endeavouring to understand the process of molecular crystallisation to the point where structural prediction is feasible. However, the topic is very complicated in that one must consider an intricate blend of contributions from efficient space packing to energetically optimised multidimensional intermolecular contacts.[1]

Gold(I) complexes of the type L–Au–X (L = neutral, X = anionic ligand) feature linear two-coordinate gold centres and are monomers in solution and in the gas phase. These molecules have considerable potential as model building blocks for supramolecular structures because of their relatively simple molecular structure and shape. Furthermore, there is growing structural evidence for ready association into dimers, oligomers and polymers as a result of attractive intermolecular Au · · · Au interactions. This aurophilic bonding in the crystalline state is associated with short, sub-van der Waals metal–metal distances (generally *ca*. 3.00 Å) and surprisingly high bond energies (5–15 kcal mol^{-1}), similar or even higher than for hydrogen bonding.[2]

As the number of characterised L–Au–X structures increases, it is hoped that clear trends will emerge regarding relationships between molecular properties (steric and electronic) and the observed supramolecularity. In contribution to this, we describe herein a series of gold(I) thiocyanate structures that exhibit aurophilic contacts. The thiocyanate anion is known to form a sharp Au–S–C angle when bound to gold(I) centres,[3] which together with the small steric influence of the neighbouring cyanide group leaves the gold atom exposed to an approach of neighbouring molecules.

Intermolecular Au · · · Au contacts involving coordinated SCN anions appear to have no precedent in the literature. $(Ph_3P)Au(SCN)$, for example, is a monomer in the crystal.[3] This could be attributed to the large size of the phosphine, although multiple phenyl embraces[4] are an alternative influence in the crystal packing of $(Ph_3P)AuX$ complexes.[3,5] The $Au(SCN)_2^-$ anion has been structurally characterised with the $AsPh_4^+$ counter cation,[6] again with no observable aurophilicity. In contrast, intramolecular Au · · · Au contacts have been observed, for example in the $[Au_4(dpmp)_2(SCN)_2]^{2+}$ [dpmp = bis(diphenylphosphinomethyl)phenylphosphine] cation.[7]

Representative neutral ligands L were chosen from the thioether, tertiary phosphine and isocyanide groups. The studied molecules therefore exhibited a variety of steric properties, which in turn led to the observation of distinctive supramolecular motifs for each. The specific donor/acceptor properties of the neutral ligands may also influence the inherent aurophilicity.

Isocyanide ligands (RNC) do not accept appreciable electron density from the metal centres to which they are attached. The RNC bonding lone pair is antibonding with respect to the C≡N bond, therefore co-ordination to metal centres characteristically results in an increase in the infrared C≡N stretching frequency.[8] For comparison, CO co-ordination is generally reliant on back donation from the metal centre into orbitals that are antibonding with respect to the C≡O bond, hence the general observation of ν(C≡O) reduction upon ligation.[9] ν(C≡N) figures have been reported for a series of ($Me_2C_6H_3$-NC)AuX (X = Cl, Br, I or CN) and $Me_2C_6H_3NC$.[10] The "free" ligand had the lowest stretching frequency, with the values for the complexes being proportional to the electronegativity of the *trans* anionic ligand. In this paper we report the crystal structure of both free 2,6-$Me_2C_6H_3NC$ and the complex (2,6-$Me_2C_6H_3NC$)Au(SCN), which allows a direct structural comparison of the isocyanide C≡N bond length.

Preparative results

The preparations of the complexes were carried out by reaction of the corresponding gold chloride complex L–Au–Cl and potassium thiocyanate in the dichloromethane–water two-phase system at room temperature, eqn. (1). The products were

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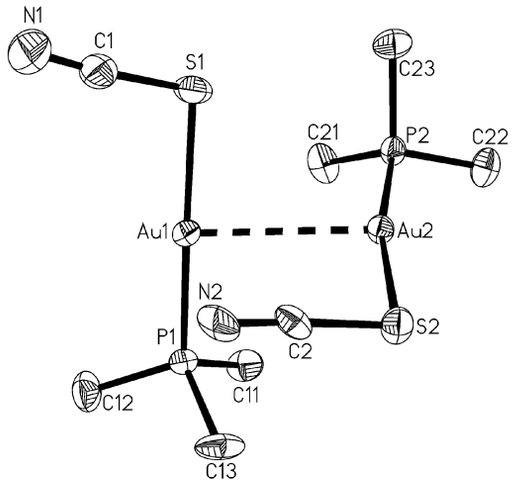

Fig. 1 Molecular structure of the dimers of compound **1** (ORTEP[11] drawing with 50% probability ellipsoids; H atoms omitted for clarity). Selected bond lengths [Å] and angles [°] (the corresponding values of the second molecule are given in parentheses): Au1 · · · Au2 3.0994(5), Au1–P1 2.263(2) [2.252(2)], Au–S1 2.334(2) [2.329(2)], S1–C1 1.673(11) [1.669(9)] and C1–N1 1.167(14) [1.160(12)]; P1–Au1–S1 175.76(8) [168.57(8)], Au1–S1–C1 102.7(3) [103.4(3)] and S1–C1–N1 175.6(10) [176.8(9)].

$$\text{L–Au–X} + \text{KSCN} \longrightarrow \text{L–Au–SCN} + \text{KCl} \qquad (1)$$

1: L = PMe_3

2: L = $S(CH_2)_4$

3: L = 2,6-$Me_2C_6H_3NC$

4: L = 2,4,6-$Me_3C_6H_2NC$

obtained in *ca.* 85% yield from the dried organic phase by precipitation with pentane. They are soluble in dichloromethane, chloroform and tetrahydrofuran, but insoluble in pentane and other non-polar solvents. The products were characterised by elemental analysis, NMR spectroscopy and mass spectrometry (see Experimental section). The crystals of all of the compounds are stable under ambient conditions, except for the thiophene complex which was stored at −25 °C in the dark.

Crystal and molecular structures

Crystals of $Me_3PAu(SCN)$ **1** are monoclinic, space group $P2_1/c$, with $Z = 8$ formula units in the unit cell. There are two independent monomers in the asymmetric unit which are associated into dimers through short aurophilic contacts [Au1 · · · Au2 3.0994(5) Å] (Fig. 1). As shown by the dihedral angle S1–Au1–Au2–S2 112.2°, the molecular axes of the two monomers are crossed, possibly in order to minimise steric repulsion. The molecular axes are both bent with angles S1–Au1–P1 175.76(8) and S2–Au2–P2 168.57(8)° to get the metal atoms closer together. The overall structural motif is similar to that of the $[(Me_3P)AuX]_2$ dimers (X = SMe[12] or I[13]).

A close inspection of the environment of the dimer **1** reveals that there are also Au · · · S contacts to neighbouring dimers, which may be significant even though the distances Au2 · · · S1′/Au2′ · · · S1 3.771(2) Å are close to the sum of the covalent radii of the partner atoms. In the resulting tetramer (Fig. 2) the atoms are related by a crystallographic centre of inversion. Other $(Me_3P)AuX$ complexes are known to form their own isostructural set (X = Cl, Br, CN, NO_3 or CF_3CO_2), in this case polymeric.[14]

Crystals of the ligand 2,6-$Me_2C_6H_3NC$ are triclinic, space group $P\bar{1}$, with $Z = 4$ formula units in the unit cell. There are

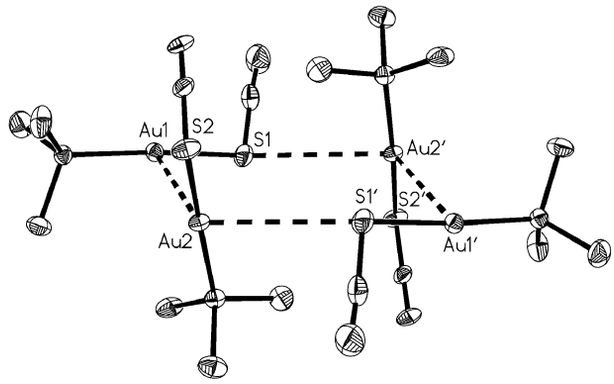

Fig. 2 Tetrameric aggregates of the dinuclear units of complex **1**. Au2 · · · S1′ 3.771(2) Å.

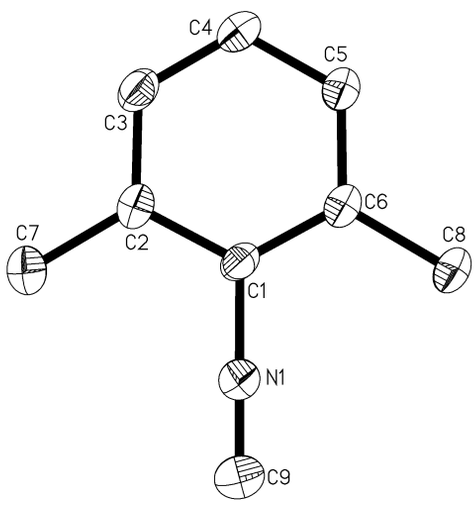

Fig. 3 Molecular structure of the ligand 2,6-$Me_2C_6H_3NC$ (only one of the two independent molecules is shown, details as in Fig. 1). Selected bond lengths [Å] and angles [°] (the corresponding values of the second molecule are given in parentheses): N1–C9 1.160(3) [1.161(2)] and N1–C1 1.399(2) [1.401(2)]; C1–N1–C9 179.4(2) [178.9(2)].

two independent molecules in the unit cell which differ only marginally in their structural details. Although not strictly imposed by crystal symmetry, the molecules obey very closely the requirements of point group C_{2v} (Fig. 3). For both molecules all non-hydrogen atoms are coplanar and each of the two methyl pairs has one hydrogen atom in the molecular plane. This conformation minimises steric repulsion between the isocyanide and the methyl groups. The axes C1–N1–C9/C10–N2–C18 are linear [179.4(2)/178.9(2)°] and the distances C9–N1/C18–N2 of the functional groups are 1.160(3)/1.161(2) Å. Both data suggest a description with sp hybridised atoms C9/C18 and N1/N2 and a high bond order, close to a triple bond. The values are similar to standard reference data.[15]

Crystals of 2,6-$Me_2C_6H_3NC$–Au–SCN **3** are triclinic, space group $P\bar{1}$, with Z = 2 molecules in the unit cell. The monomers have a seven-atom chain which is sharply bent at S1 [Au1–S1–C1 100.9(3)°] and a distinct curvature for the sequence S1–Au1–C2–N1–C3 (Fig. 4) resulting from angles S1–Au1–C2 176.0(2), Au1–C2–N1 175.5(7) and C2–N1–C3 178.4(8)°. The atoms of the seven-atom chain are all very near to the molecular plane with maximum deviations of only 0.4 Å.

The distance N1–C2 of the isocyanide group in complex **3** is 1.119(12) Å and differs very little from that in the "free" ligand. However, the data do indicate that there is a significant shortening of the isocyanide bond upon co-ordination, which is consistent with conclusions from IR vibrational studies (see Introduction).

The monomers of complex **3** are associated into centrosymmetrical dimers mainly *via* intermolecular Au–S contacts.

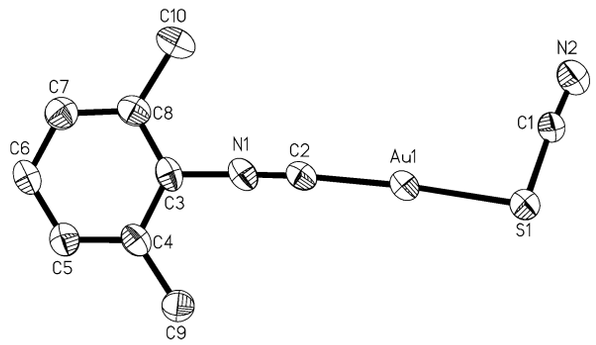

Fig. 4 Molecular structure of compound **3** (details as in Fig. 1). Selected bond lengths [Å] and angles [°]: Au1–S1 2.282(2), Au1–C2 1.970(9), S1–C1 1.672(8), C1–N2 1.160(12), C2–N1 1.119(12) and N1–C3 1.420(11); C3–N1–C2 178.4(8), N1–C2–Au1 175.5(7), C2–Au1–S1 176.0(2), Au1–S1–C1 100.9(3) and S1–C1–N2 175.7(8).

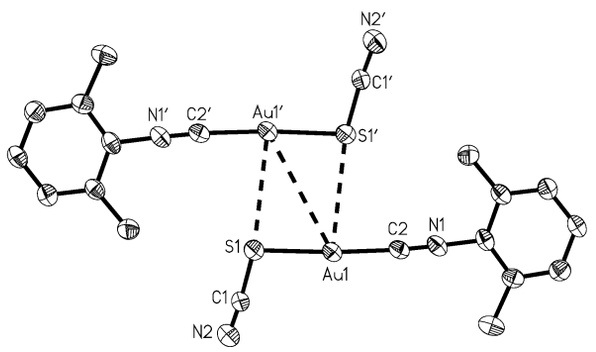

Fig. 5 Association of molecules of compound **3** into dimers. Au1 · · · S1′ 3.459(2), Au1 · · · Au1′ 3.983(1).

The atoms Au1, S1, Au1′, S1′ form a parallelogram with Au · · · S′ edges of 3.459(2) Å and an Au · · · Au′ diagonal of 3.983(1) Å (Fig. 5). This general motif was also observed for $(Me_3P)Au[SC(O)CCl_3]$,[16] which is a molecule with considerable differences in steric properties. It appears that a slippage of the two parallel L–Au–S axes in opposite directions, lengthening the Au · · · Au contacts, but shortening the Au · · · S contacts, is associated with only minor changes in energy. The nature of the substituents may therefore induce such a shift in either direction. The structure of **3** is one of seven distinct motifs observed in combination with the group $(2,6\text{-}Me_2C_6H_3NC)AuX$ (X = Cl, Br, I, CN, NO_3 or CCPh).[10,17] In contrast, $(Me_3P)AuX$ (X = Cl, Br, O_2CCF_3, CN or NO_3) and $(Bu^tNC)AuX$ (X = Cl, Br, CN or NO_3) form two isostructural series based on the steric properties of the neutral ligand.[14]

Crystals of $(2,4,6\text{-}Me_3C_6H_2NC)Au(SCN)$ **4** are also triclinic, space group $P\bar{1}$, but with four formula units in the unit cell. The asymmetric unit contains two independent molecules (Fig. 6) each of which is associated into centrosymmetrical dimers. While the two independent monomers differ very little in their structural details, their individual mode of aggregation is very different. The $Au1_2S1_2$ parallelogram has an Au1 · · · Au1′ distance of 3.397(1) Å as the shortest intermolecular contact, but in the $Au2_2S2_2$ parallelogram the corresponding distance Au2 · · · Au2′ is exceedingly long (5.125(1) Å), and contacts Au2 · · · S2′ (3.719(2) Å) are the only close approach of the two molecules (Fig. 7).

As already indicated for complex **3**, the relative positioning of the C–Au–S atom sequence of neighbouring RNC–Au–SCN molecules appears to be very flexible. Indeed, it is intriguing that introduction of only one methyl group in the *p* position (converting the 2,6-xylyl into the 2,4,6-mesityl group on going from **3** to **4**) is sufficient to induce such changes in the molecular packing.

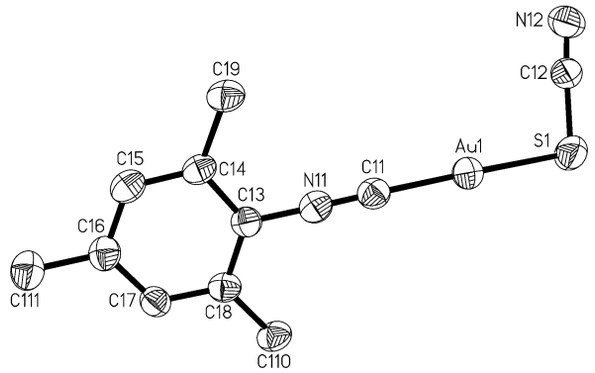

Fig. 6 Molecular structure of compound **4** (only one of the two independent molecules is shown, details as in Fig. 1). Selected bond lengths [Å] and angles [°] (the corresponding values of the second molecule are given in parentheses): Au1–S1 2.289(2) [2.284(2)], S1–C12 1.685(7) [1.685(7)], C12–N12 1.134(9) [1.156(10)], Au1–C11 1.951(7) [1.949(7)] and N11–C13 1.374(8) [1.395(9)]; C13–N11–C11 178.2(6) [177.3(6)], N11–C11–Au1 176.4(6) [178.1(6)], C11–Au1–S1 174.6(2) [176.8(2)], Au1–S1–C12 102.9(3) [101.2(3)] and S1–C12–N12 175.3(7) [174.2(7)].

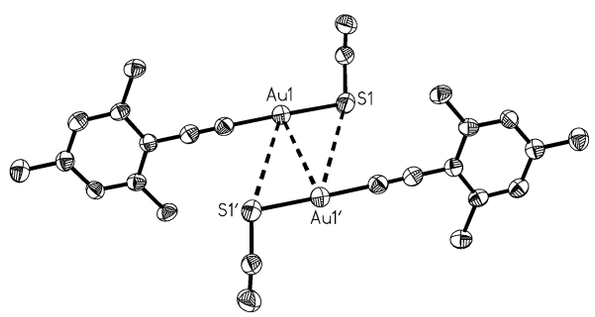

Fig. 7 Aggregation of molecules of compound **4** into dimers (only one dimer is shown, the corresponding values for the second dimer being given in parentheses). Au1 · · · S′ 3.938(2) [3.719(2)], Au1 · · · Au1′ 3.397(1) [5.125(1)] Å.

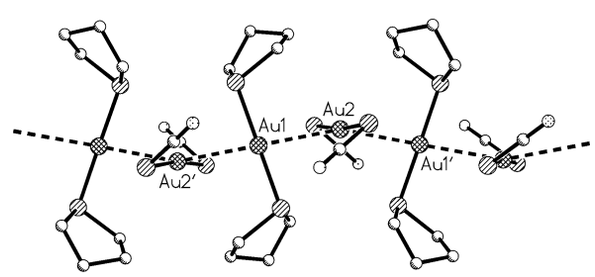

Fig. 8 The structure of compound **2** featuring a chain of cations $[(C_4H_8S)_2Au]^+$ and anions $[Au(SCN)_2]^-$. This structure is a preliminary result owing to experimental difficulties (see text). Au1 · · · Au2 3.0054 and Au1 · · · Au2′ 3.0064 Å; Au2–Au1–Au2′ 151.11 and Au1–Au2–Au1′ 158.98°.

In the crystals of complexes **1**, **3** and **4** there are no further intermolecular contacts other than those shown in Figs. 2, 5 and 7.

Crystals of compound **2** were of poor quality and did not allow an unambiguous determination of the space group. The data obtained gave a good solution in the acentric monoclinic space group *C*2 which clearly revealed the constitution of the complex (Fig. 8), but further efforts to refine the structure to a satisfactory convergence were not successful. The preliminary data show the complex to be an ionic isomer composed of bis(tetrahydrothiophene)gold(I) cations[18] and bis(thiocyanato)gold(I) anions. The $[Au(SCN)_2]^-$ anion was discovered previously, but with a distinctly different conformation (different dihedral angle C–S–Au–S–C).[6] The cations and anions alternate to form a chain with short Au · · · Au contacts of

Table 1 Crystal data for compounds **1**, **3** and **4** and 2,6-$Me_2C_6H_3NC$

	1	**3**	**4**	Ligand
Empirical formula	C_4H_9AuNPS	$C_{10}H_9AuN_2S$	$C_{11}H_{11}AuN_2S$	C_9H_9N
M	331.12	386.22	400.24	131.17
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	9.625(1)	6.077(1)	8.4855(2)	7.551(1)
b/Å	9.438(1)	8.324(1)	11.6095(3)	8.888(2)
c/Å	18.677(1)	11.000(1)	14.1815(4)	12.820(2)
α/°		98.626(2)	102.144(1)	83.39(2)
β/°	103.78(1)	95.504(2)	106.554(2)	72.87(1)
γ/°		97.452(4)	110.128(2)	64.87(1)
U/Å^3	1649.9(7)	541.67(5)	1181.65(5)	744.3(2)
Z	8	2	4	4
μ(Mo-Kα)/cm^{-1}	181.9	137.3	125.94	0.69
T/K	143	153	133	173
Measured reflections	7022	2647	26554	6437
Unique reflections	3533 [R_{int} = 0.0731]	2647	6843 [R_{int} = 0.0474]	3217 [R_{int} = 0.0474]
Refined parameters	145	128	272	254
$R1$ [$I > 2\sigma(I)$]	0.0442	0.0472	0.0445	0.0621
$wR2$	0.1104	0.1248	0.1172	0.1676

3.0054 (Au1 · · · Au2) and 3.0064 Å (Au1 · · · Au2′) and Au–Au–Au angles of 151.11° at Au1 and 158.98° at Au2.

Conclusion

Two-co-ordinate complexes, (L)AuSCN (L = tetrahydrothiophene (THT), trimethylphosphine or xylyl and mesityl isocyanide), are readily prepared in high yield by anion exchange reactions between (L)AuCl and KSCN. For each complex a different structure is observed. The crystal structure of (THT)Au(SCN) exhibits aurophilic contacts of 3.006 Å within a chain polymer of alternating cations $[(THT)_2Au]^+$ and anions $[Au(SCN)_2]^-$. Neutral molecules of (Me_3P)Au(SCN) form dimers based on Au · · · Au contacts of 3.099 Å. The overall structure appears to be tetrameric, which is possibly the result of favourable Au · · · S contacts during crystallisation. The crystal structures of (2,6-$Me_2C_6H_3NC$)Au(SCN) and (2,4,6-$Me_3C_6H_2NC$)Au(SCN) exhibit flat, centrosymmetric dimers, with relatively long intermolecular contacts. The (2,4,6-$Me_2C_6H_2NC$)Au(SCN) structure is particularly noteworthy, in that it contains two crystallographically independent dimers.

The observed structures of (2,6-$Me_2C_6H_3NC$)Au(SCN) and (2,4,6-$Me_2C_6H_2NC$)Au(SCN) appear to contain only very weak intermolecular contacts. However, the positioning of the gold and sulfur centres is proposed to be significant, particularly since the sterically distinct (Me_3P)Au[S(O)$CCCl_3$] molecule adopts a similar motif.

The comparison of non-ligated 2,6-$Me_2C_6H_3NC$ and (2,6-$Me_2C_6H_3NC$)Au(SCN) structures is consistent with the theory of isocyanide coordination to metals, in that the C≡N bond length is shorter in the complex.

Experimental

The isocyanide ligands RNC (R = xylyl or mesityl) were prepared by two-phase carbene addition.[18] (THT)AuCl was prepared by the addition of two equivalents of THT to $HAuCl_4 \cdot 3H_2O$ in MeOH.[19] The LAuCl compounds (L = Me_3P or RNC) were prepared by reaction of L with (THT)AuCl,[20] LAuSCN compounds by anion exchange during the reaction of LAuCl and KSCN in a two-phase CH_2Cl_2–water mixture.[21] Single crystals were obtained by slow diffusion of pentane into CH_2Cl_2 solutions. Crystals of 2,6-$Me_2C_6H_3NC$ were obtained by slow evaporation of a CH_2Cl_2 solution. NMR spectra (ppm) were measured from $CDCl_3$ solutions using a JEOL-GX 400 spectrometer; ^{1}H 399.8, ^{13}C-{^{1}H} 100.5, ^{31}P-{^{1}H}161.8 MHz.

Preparations

(THT)Au(SCN). To (THT)AuCl (110 mg, 0.34 mmol) in 5 mL of CH_2Cl_2 was added KSCN (33 mg, 0.34 mmol) in 5 mL of water. The two-phase mixture was stirred vigorously for three hours. The CH_2Cl_2 phase was separated, washed with 5 mL of water and dried over anhydrous $MgSO_4$. The CH_2Cl_2 phase was then treated with pentane affording a colourless, heat and/or light sensitive, solid (81 mg, 70%).

(Me_3P)Au(SCN). As for (THT)Au(SCN); from (Me_3P)AuCl (220 mg, 0.71 mmol) and KSCN (80 mg, 0.82 mmol) in 5 mL of water affording 195 mg (83%). Found: C, 15.17; H, 2.75; N, 4.05. Calc. for C_4H_9AuPNS: C, 14.50; H, 2.71; N, 4.22%. FAB-MS: *m*/*z* 273.2, $(Me_3P)Au^+$. ^{1}H NMR δ 1.5, d, ^2J(HP) 11.0 Hz, CH_3. ^{13}C-{^{1}H} NMR: δ 16.0, s, CH_3. ^{31}P-{^{1}H} NMR: δ −4.2, $P(CH_3)_3$.

(2,6-$Me_2C_6H_3NC$)Au(SCN). As for (THT)Au(SCN); from (2,6-$Me_2C_6H_3NC$)AuCl (180 mg, 0.50 mmol) and KSCN (50 mg, 0.51 mmol) in 5 mL of water affording 173 mg (90%). Found: C, 31.69; H, 2.12; N, 7.06. Calc. for $C_{10}H_9AuN_2S$: C, 31.08; H, 2.33; N, 7.25%. FAB-MS: *m*/*z* 459.6, $(2,6\text{-}Me_2C_6H_3NC)_2Au^+$. ^{1}H NMR: δ 2.53, s, *ortho*-CH_3; 7.25, d, ^3J(HH) 7.5, *meta*-H; and 7.42, d, ^3J(HH) 7.5 Hz, *para*-H. ^{13}C-{^{1}H} NMR: δ 18.7, s, CH_3; 128.0, s, *ipso*-C; 134.3, s, *ortho*-C; 128. 5, s, *meta*-C; 131.9, s, *para*-C; and 157.1, s, C≡N.

(2,4,6-$Me_2C_6H_2NC$)Au(SCN). As for (THT)Au(SCN); from (2,4,6-$Me_3C_6H_2NC$)AuCl (200 mg, 0.53 mmol) and KSCN (55 mg, 0.57 mmol) in 5 mL of water affording 180 mg (85%). Found: C, 33.78; H, 3.22; N, 7.01. Calc. for $C_{11}H_{11}AuN_2S$: C, 33.00; H, 2.75; N, 7.00%. FAB-MS: *m*/*z* 487.5, $(Mes\text{-}NC)_2Au^+$. ^{1}H NMR: δ 6.99, s, *meta*-H; 2.41, s, *ortho*-CH_3; and 2.34, s, *para*-CH_3. ^{13}C-{^{1}H} NMR: δ 121.0, t, ^1J(CN) = 13.8 Hz, *ipso*-C; 136.1, s, *ortho*-C; 129.3, s, *meta*-C; 142.3, s, *para*-C; 18.6, s, *ortho*-CH_3; and 21.5, s, *para*-CH_3.

X-Ray crystallography

Specimens of suitable size of compounds **1**, **3**, **4**, **5** and of 2,6-$Me_2C_6H_3NC$ were mounted on the ends of quartz fibers in F06206R oil and used for intensity data collection on Nonius DIP2020 (**3**, **4**, **5**) and CAD4 (**1** and 2,6-$Me_2C_6H_3NC$) diffractometers, respectively, using graphite-monochromated Mo-Kα radiation. Data of compounds **1**, **3**, and **4** were corrected for absorption effects (DELABS from PLATON).[22] The structures were solved by a combination of direct methods (SHELXS 97)[23] and Fourier-difference syntheses and refined by full matrix

least-squares calculations on F^2 (SHELXL 97).[24] The thermal motion was treated anisotropically for all non-hydrogen atoms. All hydrogen atoms were calculated and allowed to ride on their parent atoms with fixed isotropic contributions. The poor quality of the crystals of compound **5** did not allow an unambigous determination of the space group. The obtained data set gave a good solution in the acentric space group *C*2 which clearly revealed the constitution of the complex, but further efforts to refine the structure to a satisfactory convergence were not successful. Further information on crystal data, data collection and structure refinement is summarised in Table 1.

CCDC reference numbers 155748–155750 and 159216.

See http://www.rsc.org/suppdata/dt/b1/b100117p/ for crystallographic data in CIF or other electronic format.

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