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Attempted Oxidative Addition of Halogens to (Isocyanide)gold(I) Complexes[§]

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Oxidative addition of bromine to an (isocyanide)gold(I) bromide proceeds smoothly to give the corresponding (isocyanide)gold(III) tribromide as demonstrated by the preparation and structural characterization of (^{t}BuNC)AuBr$_3$. By contrast, no oxidative addition of iodine is observed with (isocyanide)gold(I) iodides. Ligand redistribution to give ionic compounds and intercalation of I$_2$ molecules occurs instead as shown for [(^{t}BuNC)$_2$Au]$^+$[AuI$_2$]$^-$ (I$_2$). In crystals of this product, linear chains of almost equidistant gold atoms of alternating cations and anions feature interionic aurophilic bonding [Au- - -Au 3.2674(5) and 3.3056(5) Å]. The iodine molecules form polyhalide bridges between the columns of complex ions. From the reaction mixture of (^{c}HexNC)AuI and an excess of iodine a crystalline pentaiodide, [(^{c}HexNC)$_2$Au]$^+$[I$_5$]$^-$, has been isolated in which the cations are imbedded between corrugated sheets of the polyhalide anions.

Introduction

Gold(I) complexes with isocyanide ligands (RNC) of the types (RNC)AuX$^{1-6}$ and [(RNC)$_2$Au]$^{+7-9}$ have recently attracted considerable interest owing to their structural diversity and physical properties (R = organic group; X = anionic ligand). Attached to gold(I) centers, isocyanides produce linear multiatomic chains which leave the coordination sphere of the metal atom wide open, thus facilitating aggregation through aurophilic bonding.[1−5,8,10−17] This type of aggregation into dimers, cyclic or open-chain oligomers, infinite chains, or layers is often associated with new colligative properties including in particular tunable luminescence.[3,4,7,18,19] Self-assembly into liquid crystalline or rotatory phases[6,19] as well as into intriguing catenanes has also been observed with various modes of connectivity.[15,20−27]

(Isocyanide)gold(I) complexes may further be used for the preparation of carbene complexes of gold[28−33] and as catalysts for organic transformations.[34,35] Complexes with small ligands are volatile and can be employed as precursors for the chemical vapor deposition of thin films of gold metal.[36,37] There is a substantial literature

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[§] Dedicated to Professor Herbert Schumann on the occasion of his retirement.

(1) Humphrey, S. M.; Mack, H.-G.; Redshaw, C.; Elsegood, M. R. J.; Young, K. J. H.; Mayer, H. A.; Kaska, W. C. *Dalton Trans.* **2005**, 439.

(2) Siemeling, U.; Rother, D.; Bruhn, C.; Fink, H.; Weidner, T.; Traeger, F.; Rothenberger, A.; Fenske, D.; Priebe, A.; Maurer, J.; Winter, R. *J. Am. Chem. Soc.* **2005**, *127*, 1102−1103.

(3) Elbjeirami, O.; Omary, M. A.; Stender, M.; Balch, A. L. *Dalton Trans.* **2004**, 3173−3175.

(4) White-Morris, R. L.; Olmstead, M. M.; Balch, A. L.; Elbjeirami, O.; Omary, M. A. *Inorg. Chem.* **2003**, *42*, 6741.

(5) Liau, R.-Y.; Mathieson, T.; Schier, A.; Berger, R. J. F.; Runeberg, N.; Schmidbaur, H. *Z. Naturforsch.* **2002**, *57b*, 881.

(6) Schmidbaur, H. *Nature* **2001**, *413*, 32.

(7) White-Morris, R. L.; Olmstead, M. M.; Balch, A. L. *J. Am. Chem. Soc.* **2003**, *125*, 1033−1040.

(8) Mathieson, T. J.; Langdon, A. G.; Milestone, N. B.; Nicholson, B. K. *Dalton Trans.* **1999**, 201.

(9) Schneider, W.; Sladek, A.; Bauer, A.; Angermaier, K.; Schmidbaur, H. *Z. Naturforsch.* **1997**, *52b*, 53−56.

(10) Wilton-Ely, J. D. E. T.; Schier, A.; Schmidbaur, H. *Organometallics* **2001**, *20*, 1895−1897.

(11) Wilton-Ely, J. D. E. T.; Ehlich, H.; Schier, A.; Schmidbaur, H. *Helv. Chim. Acta* **2001**, *84*, 3216.

(12) Mathieson, T.; Schier, A.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **2001**, 1196−1200.

(13) Mathieson, T.; Schier, A.; Schmidbaur, H. *Dalton Trans.* **2000**, 3881−3884.

(14) Ecken, H.; Olmstead, M. M.; Noll, B. C.; Attar, S.; Schlyer, B.; Balch, A. L. *Dalton Trans.* **1998**, 3715.

(15) Bayon, R.; Coco, S.; Espinet, P.; Fernández-Mayordomo, C.; Martin-Alvarez, J. M. *Inorg. Chem.* **1997**, *36*, 2329.

(16) Schneider, W.; Angermaier, K.; Sladek, A.; Schmidbaur, H. *Z. Naturforsch.* **1996**, *51b*, 790.

(17) Eggleston, D. S.; Chodosh, D. F.; Webb, R. L.; Davis, L. L. *Acta Crystallogr.* **1986**, *42c*, 36−38.

(18) Balch, A. L. *Gold Bull.* **2004**, *37*, 45−50.

(19) Bachman, R. E.; Bodolosky-Bettis, S. A.; Glennon, S. C.; Sirchio, S. A. *J. Am. Chem. Soc.* **2000**, *122*, 7146−7147.

(20) Espinet, P. *Gold Bull.* **1999**, *32*, 127.

(21) Benouazzane, M.; Coco, S.; Espinet, P.; Martin-Alvarez, J. M. *J. Mater. Chem.* **1999**, *9*, 2327.

(22) Alejos, P.; Coco, S.; Espinet, P. *New J. Chem.* **1995**, *19*, 799−805.

(23) Benouazzane, M.; Coco, S.; Espinet, P.; Martin-Alvarez, J. M. *J. Mater. Chem.* **1995**, *5*, 441−445.

(24) Ishii, R.; Kaharu, T.; Pirio, N.; Zhang, S.-W.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1215−1216.

(25) Kaharu, T.; Ishii, R.; Adachi, T.; Yoshida, T.; Takahashi, S. *J. Mater. Chem.* **1995**, *5*, 687.

(26) Kaharu, T.; Ishii, R.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1994**, 1349−1350.

(27) Espinet, P.; Esteruelas, M. A.; Oro, L. A.; Serrano, J. L.; Sola, E. *Coord. Chem. Rev.* **1992**, *117*, 215−274.

(28) Zhang, S.-W.; Ishii, R.; Takahashi, S. *Organometallics* **1997**, *16*, 20−26.

(29) Bandini, A. L.; Banditelli, G.; Minghetti, G.; Pelli, B.; Traldi, P. *Organometallics* **1989**, *8*, 590−593.

(30) Minghetti, G.; Bonati, F.; Banditelli, G. *Inorg. Chem.* **1976**, *15*, 1718−1720.

(31) Minghetti, G.; Bonati, F. *J. Organomet. Chem.* **1973**, *54*, C62.

(32) Bonati, F.; Minghetti, G. *Gazz. Chim. Ital.* **1973**, *103*, 373−386.

(33) Bonati, F.; Minghetti, G. *Synth. React. Inorg. Met.-Org. Chem.* **1971**, *1*, 299−302.

(34) Ito, Y.; Sawamura, M.; Hayashi, T. *J. Am. Chem. Soc.* **1986**, *108*, 6405−6406.

(35) Togni, A.; Pastor, S. D. *J. Org. Chem.* **1990**, *55*, 1649−1664.

(36) Norton, P. R.; Young, P. A.; Cheng, Q.; Dryden, N.; Puddephatt, R. J. *Surf. Sci.* **1994**, *307*, 172−176.

(37) Dryden, N. H.; Shapter, J. G.; Coatsworth, L. L.; Norton, P. R.; Puddephatt, R. J. *Chem. Mater.* **1992**, *4*, 979−981.

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on isocyanide complexes of gold*aryls* and -*alkynyls*, which is not considered any further in the present context.[38]

Structural and quantum-chemical studies have shown that aurophilic bonding between complexes (RNC)AuX can give rise to a wide range of intermetallic distances (Au- - -Au contacts between 2.9 and 3.6 Å) and dihedral angles (CAu- - -AuC), the latter indicating a parallel orientation or a crossing of the molecular axes.[5] From these data and from the theoretical calculations it appears that the bonding on one hand is generally weaker than, for example, in the corresponding phosphine complexes (R_3P)AuX, but on the other hand is more strongly influenced by the co-ligand X. Even for the small halide series (X = Cl, Br, I) there are large differences in the structural motifs and in the calculated binding energies, and this is even more true for nitrates and carboxylates.

Because these differences in mutual affinity of (RNC)-AuX complexes should also be reflected by the *redox behavior* of the complexes, we have recently investigated the oxidative addition of halogens X_2 to these substrates. The reactions can lead to the first (RNC)AuX_3 complexes, which to date have only been described in passing and without giving any details.[39] The only other known (isocyanide)gold(III) complexes contain at least one alkyl or aryl group.[15,40−42]

The work presented in this account is an extension of studies on the related complexes with tertiary phosphines.[43,44] In compounds of the type (R_3P)AuX the reactivity is strongly influenced by the steric effects of the phosphine ligands which are close to the metal center. In the isocyanide analogues the steric effect should be negligible owing to the more remote position of the group R.

Preparative Studies

(Isocyanide)gold(I) halides are readily obtained by the reaction of the dimethyl sulfide[32] or tetrahydrothiophene[11] complexes with the appropriate isocyanide. The chlorides are generally prepared first and then converted into the bromides or iodides.[16] (No fluorides are known.)

The first complexes of the type (RNC)$AuCl_3$ mentioned in the literature (R = Ph, *p*-Tol) were prepared in low yield by reaction of isocyanides with $HAuCl_4$ in ethanol.[39] No oxidative addition of chlorine to the gold(I) chloride complex was attempted.

In the present study, three *bromide* complexes of the type (RNC)AuBr, with R = Me, ^{c}Hex, and ^{t}Bu, were reacted with an equimolar quantity of bromine in dichloromethane at −30 °C. Deep red solutions were obtained out of which red solids could be precipitated by addition of pentane. Their IR spectra showed several bands in the region of C≡N stretching frequencies, indicating that mixtures of products were present. This result was confirmed by the microanalytical data, which could not be assigned to a 1:1 or 1:3 stoichiometry (Au: Br). The results suggest that equilibria are established in the reaction mixtures involving gold(I) and gold(III) complexes, the latter losing bromine in a vacuum at or above room temperature. Neutral species (RNC)AuBr/(RNC)$AuBr_3$ and ions $[(RNC)_2Au]^+/[AuBr_2]^-/[AuBr_4]^-$ may be present, of which the former three give rise to several IR absorptions.

It was only in the case of the system with the ^{t}BuNC ligand that a pure component could be crystallized (from dichloromethane/pentane at −30 °C, 65% yield) and identified as (^{t}BuNC)$AuBr_3$ by elemental analysis, spectroscopic data, and a single-crystal X-ray analysis (below). The orange-red crystals decompose at 80 °C and have an IR absorption ν(C≡N) at 2282 cm^{-1}, clearly shifted from 2235 cm^{-1} for the (^{t}BuNC)AuBr complex (in KBr).[16]

For the *iodide* complexes (RNC)AuI with R = Me, ^{c}Hex, and ^{t}Bu no evidence was obtained for oxidative addition of *iodine* to give any gold(III) complexes. In the first case, only the starting material (MeNC)AuI was recovered. From the experiments with (^{c}HexNC)AuI, an adduct of the net composition $(^c\mathrm{HexNC})_2AuI_5$ was isolated in low yield in the form of black crystals. (The byproducts were not identified.) The similarity of its NMR and IR data with those of the (^{c}HexNC)AuI precursor[4] suggested that the isocyanide ligands are attached to gold(I) centers and that only a polyiodide was formed. This situation was confirmed by an X-ray diffraction analysis, which identified the product as the ionic compound $[(^c\mathrm{HexNC})_2Au]^+I^-(I_2)_2$ (below). An ionic polyiodide was also obtained starting from (^{t}BuNC)AuI. Deep red crystals of the composition $(^t\mathrm{BuNC})_2Au_2I_4$ were isolated and identified as $[(^t\mathrm{BuNC})_2Au]^+[AuI_2]^-(I_2)$.

Structural Studies

(Isocyanide)gold(III) trihalides (RNC)AuX_3 have not previously been structurally characterized. Therefore the structure of (^{t}BuNC)$AuBr_3$ has now been determined. The red crystals of this compound (from dichloromethane/pentane at 20 °C) are orthorhombic (space group *Pnma*, *Z* = 4) and contain discrete molecules with the gold atom in an almost ideal square planar coordination (Figure 1). All heavy atoms except for the carbon atoms C4/C4′ are situated in a crystallographically imposed mirror plane. One of the two *cis* bromine atoms (Br1) is therefore eclipsed with a carbon atom of the isocyanide (C3), while the other (Br3) is staggered relative to the carbon atoms C4/C4′. However, considering the long distance between bromine atoms and methyl groups, this conformation is probably not determined by intramolecular steric interactions. It is more likely that it has its origin in molecular packing (below).

Notably, from the Au−Br distances it appears that the isocyanide ligand has a strengthening *trans*-influence on the Au1−Br2 bond [2.395(1) Å], but a labilizing *cis*-influence on the bonds Au1−Br1/Br3 [2.434(1) and 2.421(1) Å, respectively].

The complexes are stacked along the *b*-axis of the crystal with neighboring molecules having their main

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[38] Schmidbaur, H.; Grohmann, A.; Olmos, M. E. In *Gold: Progress in Chemistry, Biochemistry and Technology*; Schmidbaur, H., Ed.; Wiley: Chichester, 1999; p 647.

[39] Sacco, A.; Freni, M. *Gazz. Chim. Ital.* **1956**, *86*, 195−198.

[40] Uson, R.; Laguna, A.; Laguna, M.; Fernandez, E.; Jones, P. G.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1971−1976.

[41] Uson, R.; Laguna, A.; Bergareche, B. *J. Organomet. Chem.* **1980**, *184*, 411−416.

[42] Uson, R.; Laguna, A.; Vicente, J.; Garcia, J.; Bergareche, B.; Brun, P. *Inorg. Chim. Acta* **1978**, *28*, 237−243.

[43] Schneider, D.; Schuster, O.; Schmidbaur, H. *Dalton Trans.* **2005**, 1940−1947.

[44] Schneider, D.; Schier, A.; Schmidbaur, H. *Dalton Trans.* **2004**, 1995.

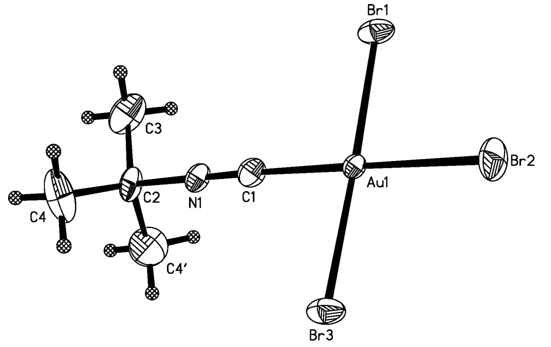

Figure 1. Molecular structure in crystals of (^{t}BuNC)AuBr$_3$ (ORTEP, 50% probability ellipsoids). Selected bond lengths [Å] and angles [deg]: Au1−C1 1.991(10), N1−C1 1.127(12), N1−C2 1.482(11), Au1−Br1 2.434(1), Au1−Br2 2.395(1), Au1−Br3 2.421(1); N1−C1−Au1 178.0(9), C1−N1−C2 179.9(10), C1−Au1−Br1 89.4(3), C1−Au1−Br2 179.5(3), C1−Au1−Br3 88.5(3), Br1−Au1−Br2 91.1(1), Br1−Au1−Br3 178.0(1).

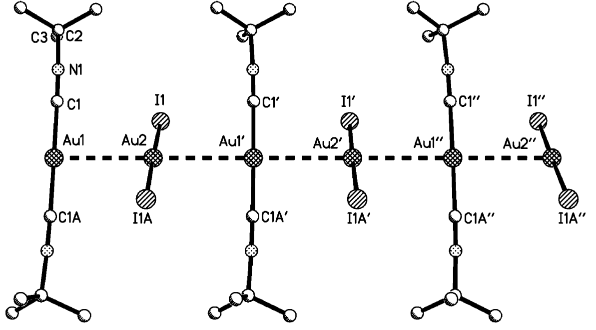

Figure 2. Assembly of cation and anion of [(^{t}BuNC)$_2$Au]$^+$[AuI$_2$]$^-$ (I$_2$) along the *b*-axis of the crystal (arbitrary radii, hydrogen atoms omitted). The linear infinite chain of gold atoms has the charge sequence $[+ - + -]_n$. Selected bond lengths [Å] and angles [deg]: Au1−Au2 3.306(1), Au2−Au1′ 3.267(1), 1.980(9), N1−C1 1.145(11), Au2−I1 2.553(1); C1−Au1−C1A 179.5(4), C1−Au1−Au2 90.3(2), Au1−Au2−Au1′ 180, I1−Au2−I1A 179.0(1), I1−Au2−Au1 90.5(1), C1−Au1−Au2−I2 42.9(2).

axis in an antiparallel orientation. The shortest intermolecular contacts are the distances Au1−Br1′ of 3.537(1) Å, only insignificantly shorter than the sum of the van der Waals radii (ca. 3.60 Å). There may be a contribution to the stability of the lattice from distant C−H- - -Br contacts, but this aspect was not analyzed any further owing to the uncertainty of the hydrogen positions. The distance Au1−Au1′ of 4.105(1) Å is too long to consider any aurophilic bonding. It has generally been observed that metallophilic bonding between heavy metal atoms in higher oxidation states is negligible.[45]

The compound of the composition (^{t}BuNC)$_2$Au$_2$I$_4$ obtained from (^{t}BuNC)AuI and iodine has been shown to feature ionic components with intercalated iodine molecules: [(^{t}BuNC)$_2$Au]$^+$[AuI$_2$]$^-$ (I$_2$). The red crystals (from dichloromethane/pentane at −30 °C) are monoclinic (space group *C*2/*c*, *Z* = 4) with linear strings of gold atoms formed by aurophilic bonding between alternating cations and anions running parallel to the *b*-axis (Figure 2). The gold atoms are in special positions with their two ^{t}BuNC ligands or iodine atoms, respectively, related by a 2-fold axis. The Au- - -Au contacts alternate in length with Au1−Au2 = 3.306(1) and Au2−Au1′ = 3.267(1) Å. The I−Au−I and C−Au−C axes are rotated against each other by a dihedral angle C1−Au1−Au2−I1 of 42.9(2)°.

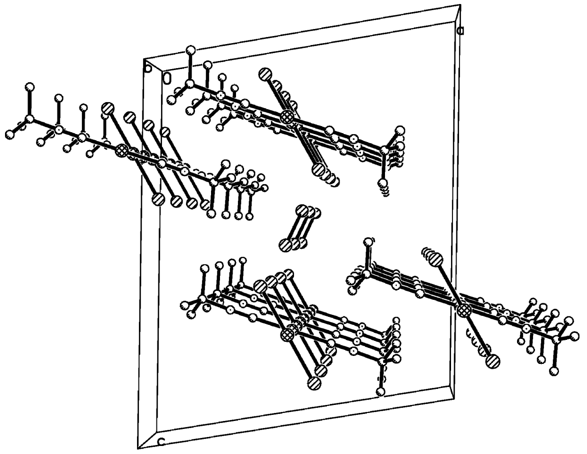

Figure 3. Unit cell of the crystal of [(^{t}BuNC)$_2$Au]$^+$[AuI$_2$]$^-$ (I$_2$) showing the position of the intercalated I$_2$ molecules, viewed along the *b*-axis (arbitrary radii, hydrogen atoms omitted). For the atomic numbering of the ion chains, see Figure 2. The atoms of the I$_2$ molecule are labeled I2/I2A. Selected bond lengths [Å] and angles [deg]: I2−I2A 2.738(1), I1−I2 3.424(1); Au2−I1−I2 145.9(1).

The overall arrangement of the components in the cation/anion chains is reminiscent of the structure of [Mes$_2$Au]$^+$[Au(GeCl$_3$)$_2$]$^-$,[46] but in this analogue the Au- - -Au contacts are equidistant and the dihedral angle C−Au−Au−Ge is 90° (by symmetry).

The intercalated iodine molecules reside on centers of inversion and have I- - -I contacts with a distance of 3.424(1) Å (Figure 3), typical for metal polyiodide compounds.[44,47−49] The significance of potential C−H- - -Au/I contacts for the molecular packing has not been investigated.

The black crystals of the composition (^{c}HexNC)$_2$AuI$_5$ obtained from (^{c}HexNC)AuI and excess iodine have been shown to contain [(^{c}HexNC)$_2$Au]$^+$ cations and corrugated polyiodide sheets (Figure 4). The cations are disordered over two positions, which could be accounted for by a model with 50:50 occupancy. The individual cation has two symmetry-related ligands and is bent with an angle C1−Au1−C1′ of 171.3(6)°. There are no aurophilic contacts between cations.

In the corrugated polyiodide layers, the iodide anion (I2) is surrounded by four iodine molecules with distances I1- - -I2 and I2- - -I3 of 3.331(1) and 3.334(1) Å, respectively. For comparison, the internal distances of the two nonequivalent I$_2$ molecules are typically 2.764(1) and 2.773(1) Å for I1−I1A and I3−I3A, respectively. The angles I1−I2−I1′and I3−I2−I3′ are 176.3(1)° and 135.7(1)°, of which the latter is the main reason for the folding of the polyiodide sheets.

Discussion

The present study has shown that (isocyanide)gold(I) bromides are readily oxidized by bromine Br$_2$ in

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(45) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597.

(46) Bauer, A.; Schneider, W.; Schmidbaur, H. *Inorg. Chem.* **1997**, *36*, 2225−2226.

(47) Castro-Castro, L. M.; Guloy, A. M. *Inorg. Chem.* **2004**, *43*, 4537.

(48) Svensson, P. H.; Kloo, L. *Chem. Rev.* **2003**, *103*, 1649.

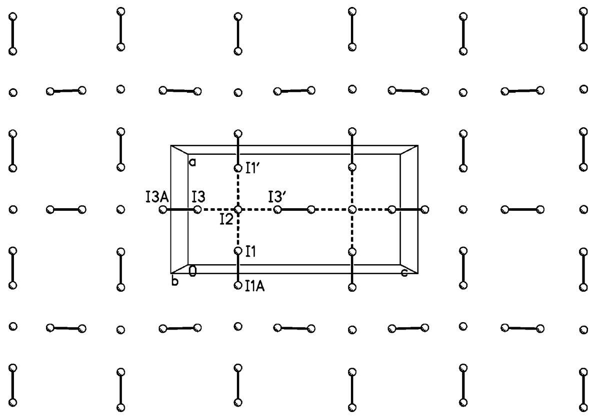

Figure 4. Projection on the *ac* plane of the unit cell of a crystal of $[(^cHexNC)_2Au]^+[I]^-$ $(I_2)_2$, showing only one polyiodide layer (arbitrary radii, cations omitted). Each iodide anion I2 has contacts to four I_2 molecules. Selected bond lengths [Å] and angles [deg]: I2−I1 3.331(1), I2−I3 3.334(1), I1−I1A 2.764(1), I3−I3A 2.773(1); I1−I2−I1′ 176.3(1), I3−I2−I3′ 135.7(1), I1−I2−I3 89.5(1), I1′−I2−I3 72.5(1).

dichloromethane to give (isocyanide)gold(III) tribromides. As demonstrated by a structure determination of $(^tBuNC)AuBr_3$, the gold atom is in a square planar coordination with longer and probably more labile *cis*-AuBr bonds as compared to the *trans*-AuBr bond.

By contrast, under similar reaction conditions (isocyanide)gold(I) iodides do not undergo oxidative addition of iodine I_2. Instead, a ligand redistribution takes place giving ionic compounds with a homoleptic substitution pattern for the cations and the anions. In the crystalline products obtained from the reaction mixtures, the iodine is intercalated by the gold(I) complexes in what can be referred to as gold(I) polyiodides. The structure has been determined for the examples $(^tBuNC)_2Au_2I_4$ and $(^cHexNC)_2AuI_5$ identified as $[(^tBuNC)_2Au]^+[AuI_2]^-$ (I_2) and $[(^cHexNC)_2Au]^+[I]^-$ $(I_2)_2$, respectively.

Aurophilic contacts are not discernible in the gold(III) tribromide complex $(^tBuNC)AuBr_3$, but they are highly significant for the assembly of the components in crystals of the gold(I) complex $[(^tBuNC)_2Au]^+[AuI_2]^-$ (I_2). The gold atoms are lined up in linear strings formed from alternating cations and anions. The Au- - -Au contacts of 3.306(1) and 3.267(1) Å are clearly indicative of significant interactions.[50] The iodine molecules are intercalated between these strings with conventional Au−I- - -I−I polyiodide bonding.[48]

In their reactivity with the two heavy halogens, the (isocyanide)gold(I) bromides and iodides thus behave very similarly to the corresponding complexes of tertiary phosphines $(R_3P)AuBr/I$.[43,44] The same reactivity pattern is also valid for most of the gold(I) pseudohalides as recently demonstrated for the acetylides.[51,52]

Table 1. Crystal Data, Data Collection, and Structure Refinement

	$(^tBuNC)AuBr_3$	$(^tBuNC)_2Au_2I_4$	$(^cHexNC)_2AuI_5$
		Crystal Data	
formula	$C_5H_9AuBr_3N$	$C_{10}H_{18}Au_2I_4N_2$	$C_{14}H_{22}AuI_5N_2$
M_r	519.83	1067.80	1049.80
cryst syst	orthorhombic	monoclinic	orthorhombic
space group	*Pnma*	*C*2/*c*	*Cmcm*
a (Å)	9.9010(2)	16.1578(6)	9.3917(2)
b (Å)	6.9290(1)	6.5733(3)	14.2228(3)
c (Å)	16.5575(3)	19.8037(9)	18.0534(3)
α (deg)	90	90	90
β (deg)	90	100.2835(17)	90
γ (deg)	90	90	90
V (Å^3)	1135.91(3)	2069.56(15)	2411.51(8)
ρ_{calc} (g cm^{-3})	3.040	3.427	2.892
Z	4	4	4
F(000)	920	1848	1856
μ(Mo Kα) (cm^{-1})	23.446	20.117	12.501
		Data Collection	
T (°C)	−130	−130	−130
no. of measd reflns	25 511	32 730	29 072
no. of unique reflns	1134 [R_{int} = 0.076]	1916 [R_{int} = 0.084]	1209 [R_{int} = 0.036]
absorp corr	DELABS	DELABS	DELABS
T_{min}/T_{max}	0.390/0.790	1.776/0.706	0.866/0.562
		Refinement	
no. of refined params	61	83	73
R1	0.0277	0.0365	0.0224
wR2 [$I > 2\sigma(I)$][a]	0.0640	0.0978	0.0527
a/*b*	0.0217/9.1996	0.0554/10.6570	0.082/19.7546
ρ_{fin}(max/min) (e Å^{-3})	2.658/−1.121	1.945/−1.847	0.576/−0.654

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

Experimental Section

All experiments were carried out in an atmosphere of pure and dry nitrogen. Glassware was oven-dried and filled with nitrogen, and solvents were dried, distilled, and saturated with nitrogen. Standard equipment was used throughout. IR spectra were measured on a Jasco FT-IR 460 Plus spectrometer. NMR spectra were obtained at room temperature on JEOL-400 or JEOL-270 spectrometers. Chemical shifts are reported in *δ* values [ppm] relative to the residual solvent resonances (^1H, ^{13}C). $^{31}P\{^1H\}$ NMR spectra are referenced to external aqueous H_3PO_4 (85%). Coupling constants *J* are given in Hz. The reagents were commercially available or prepared following literature procedures: $(^tBu\text{-}NC)AuBr$,[16] $(MeNC)AuBr$,[53] $(^cHexNC)AuBr$,[4] $(^tBuNC)AuI$,[5] $(MeNC)AuI$,[16] and $(^cHexNC)AuI$.[4]

$(^tBuNC)AuBr_3$. $(^tBuNC)AuBr$ (300 mg, 0.83 mmol) was dissolved in 25 mL of dichloromethane at −30 °C, and Br_2 (133 mg, 0.83 mmol) was added slowly. The red solution was stirred for 1 h before the volume of the solvent was reduced to about 5 mL in vacuo. The crude product was precipitated with 50 mL of *n*-pentane. Recrystallization by slow diffusion of *n*-pentane into a saturated dichloromethane solution at −30 °C gave 160 mg (65% yield) of a red crystalline product, mp (dec) 80 °C. ^1H NMR (CD_2Cl_2, 25 °C): *δ* 1.61 [s, $(H_3C)_3C$]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, RT): *δ* 29.5 [s, $(H_3C)_3C$], 58.3 $(H_3C)C$, ^tBuNC was not detected. IR (KBr) [cm^{-1}]: 2282 (s), $\nu(N{\equiv}C)$. Anal. Calc for $C_5H_9AuBr_3N$ (519.83 g·mol^{-1}): C, 11.55; H, 1.75; N, 2.69; Br, 46.1. Found: C, 11.68; H, 1.83: N, 2.78; Br, 44.9.

$(^cHexNC)AuBr + Br_2$. $(^cHexNC)AuBr$ (300 mg, 0.78 mmol) and Br_2 (125 g, 0.78 mmol) were dissolved in 15 mL of dichloromethane, and the reaction mixture was stirred for 1 h at −30 °C. Then the solvent was evaporated under reduced pressure to a volume of 2 mL, and 50 mL of *n*-pentane was added to precipitate a red, nonstoichiometric solid. ^1H NMR (CD_2Cl_2, 25 °C): *δ* 1.99−1.53 [m, ^cHexNC]. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): *δ* 58.0 [t, $^1J_{CN}$ = 5.4 Hz, C1], 31.3 [s, C2], 24.7 [s, C3], 22.5 [s, C4]; ^cHexNC was not detected. IR (KBr) [cm^{-1}]: 2360 (w), byproduct; 2287 (s) $\nu(N{\equiv}C)$.

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(49) Svensson, P. H.; Rosdahl, J.; Kloo, L. *Chem. Eur. J.* **1999**, *5*, 305.

(50) Schmidbaur, H. *Gold Bull.* **2000**, *33*, 3.

(51) Schuster, O.; Liau, R.-Y.; Schier, A.; Schmidbaur, H. *Inorg. Chim. Acta* **2005**, *358*, 1429−1441.

(52) Schuster, O.; Schmidbaur, H. *Organometallics* **2005**, *24*, 2289−2296.

(53) Browning, J.; Goggin, P. L.; Goodfellow, R. J. *J. Chem. Res., Synop.* **1978**, 328−329.

(MeNC)AuBr + Br$_2$. (MeNC)AuBr (200 mg, 0.63 mmol) was dissolved in dichloromethane (10 mL) at −30 °C, and Br$_2$ (100 mg, 0.63 mmol) was added. The solution was stirred for 1 h before the solvent was evaporated slowly to leave a volume of 2 mL. Addition of *n*-pentane (40 mL) yielded a red, nonstoichiometric product. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ 3.76 [br s, *Me*NC]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ 31.7 [t, $^1J_{CN}$ = 7.7 Hz, *Me*NC], MeN*C* was not detected. IR (KBr) [cm^{-1}]: 2360 (m), byproduct; 2275 (s) ν(N≡C).

[(^{t}BuNC)$_2$Au]$^+$[AuI$_2$]$^-$ (I$_2$). (^{t}BuNC)AuI (200 mg, 0.49 mmol) and I$_2$ (124 mg, 0.49 mmol) were dissolved in 10 mL of dichloromethane at 20 °C, and the reaction mixture was stirred for 3 h. Crystallization was initiated by slow diffusion of *n*-pentane at −30 °C. After a few weeks 180 mg (69% yield) of red crystals was collected, mp (dec) 64 °C. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ 1.55 [s, (H_3C)$_3$C]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ 59.3 [s, (H$_3$C)*C*], 30.0 [s, (H$_3$*C*)$_3$C]; ^{t}BuN*C* was not detected. IR (KBr) [cm^{-1}]: 2234 (s), ν(*N*≡*C*). Anal. Calc for $C_{10}H_{18}Au_2I_4N_2$ (1067.80 g·mol^{-1}): C, 11.25; H, 1.70; N, 2.62; I, 47.5. Found: C, 11.13; H, 1.81; N, 2.74; I, 45.9.

[(^{c}HexNC)$_2$Au]$^+$[I]$^-$ (I$_2$)$_2$. (^{c}HexNC)AuI (200 mg, 0.46 mmol) was dissolved in dichloromethane (15 mL), I$_2$ (117 mg, 0.46 mmol) was added, and the mixture was stirred for 3 h at 20 °C. Pentane vapor was allowed to condense into the solution at −30 °C. Black crystals (61 mg, 13% yield, calc for Au) were filtered off, mp (dec) 45 °C. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ 2.00−1.46 [m, ^{c}HexNC]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ 55.3 [t, $^1J_{CN}$ = 5.4 Hz, C1], 31.7 [s, C2], 24.9 [s, C3], 23.0 [s, C4]; ^{c}HexN*C* was not detected. IR (KBr) [cm^{-1}]: 2242 (s), ν(*N*≡*C*). Anal. Calc for $C_{14}H_{22}AuI_5N_2$ (1049.80 g·mol^{-1}): C, 16.02; H, 2.11; N, 2.67. Found: C, 15.22; H, 1.97; N, 2.45.

(MeNC)AuI + I$_2$. (MeNC)AuI (100 mg, 0.27 mmol) was treated with I$_2$ (69 mg, 0.27 mmol) in 10 mL of dichloromethane for 3 h at 20 °C. Evaporation of the solvent to a volume of about 2 mL and addition of 50 mL of *n*-pentane gave a black solid with nonstoichiometric composition. ^{1}H NMR (CD$_2$Cl$_2$, 25 °C): δ 3.40 [br s, *Me*NC]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25 °C): δ 29.8 [t, $^1J_{CN}$ = 8.5 Hz, *Me*NC]; MeN*C* was not detected. IR (KBr) [cm^{-1}]: 2269 (s), ν(N≡C).

Crystal Structure Determinations. 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 (l = 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).[54] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model with fixed isotropic contributions. Further information on crystal data, data collection, and structure refinement are summarized in Table 1. Important interatomic distances and angles are shown in the corresponding figure captions. Complete lists of displacement parameters and tables of interatomic distances and angles have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. The data are available on request on quoting CCDC 270211−270213.

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Supporting Information Available: Two additional figures pertaining to the crystal structure of (^{c}HexNC)$_2$AuI$_5$. Details of crystal data, data collection, and structure refinement, tables of atomic coordinates, isotropic and anisotropic thermal parameters, and bond lengths and angles are available free of charge via the Internet at http://pubs.acs.org.

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[54] Sheldrick, G. M. *SHELX-97: Programs for Crystal Structure Analysis*; University of Göttingen: Germany, 1997.