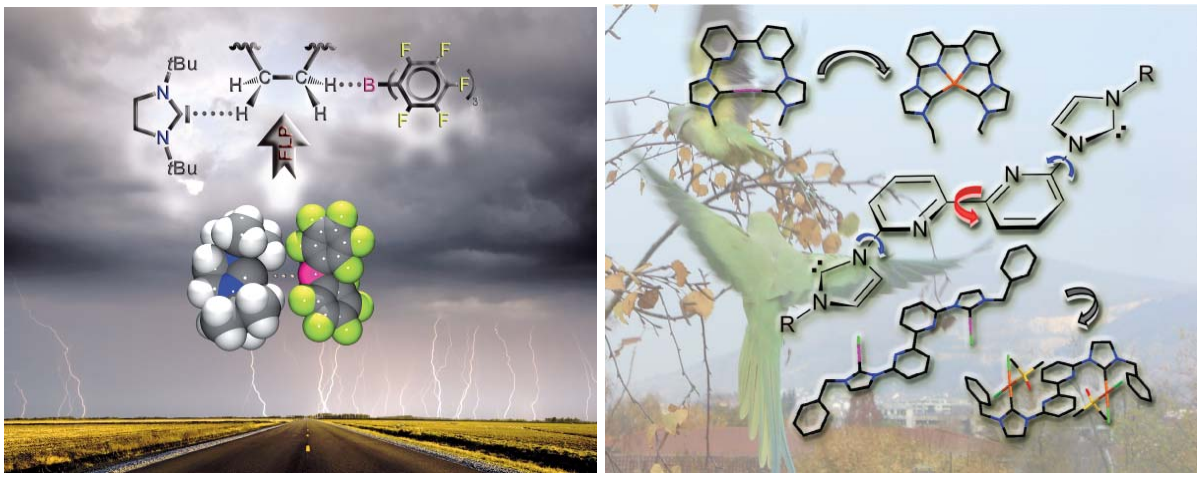
This paper is published as part of a *Dalton Transactions* themed issue on:

N-Heterocyclic Carbenes

Guest Editor Ekkehardt Hahn

Westfälische Wilhelms-Universität, Münster, Germany

Published in issue 35, 2009 of *Dalton Transactions*



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One-step formation of cyclometallated Au(III) *N,S*-heterocyclic carbene: crystallographic analysis†

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Received 15th May 2009, Accepted 13th July 2009
First published as an Advance Article on the web 30th July 2009
DOI: 10.1039/b909661b

Gold(I) *N,S*-heterocyclic carbene AuBr(NSHC) (NSHC = *N*-allylbenzothiazolin-2-ylidene) (**1**) with an allyl pendant is oxidised by iodine to give $[AuI_2(NSHC)_2]^+[I_3]^-$ (**2**) and a cyclometallated byproduct $AuBr_2(\eta\text{-}C_6H_4SCNCH_2CHCH_2Br\text{-}C,C')$ (**3**). The latter can be prepared directly from bromination of **1**. Similar reaction with the crotyl (but-2-en-1-yl) derivative AuBr(NSHC) (NSHC = *N*-crotylbenzothiazolin-2-ylidene) (**4**) gives an oxidative addition product $AuBr_3(C_6H_4SCNCH_2CH{=}CHCH_3)$ (**5**). X-Ray single-crystal crystallographic analysis of **3** reveals a 5-membered cyclometallated ring in a sq planar metal that gives two types of Au^{III}–C bonds. Similar structural analysis has also been carried out in **1**, **2** and **5**.

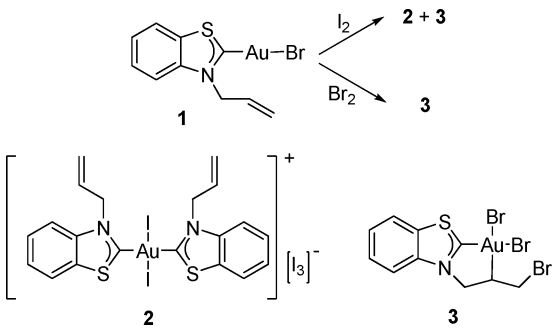
Introduction

The recent emergence of gold carbenes[1] is one of the key highlights of *N*-heterocyclic carbene (NHC) chemistry.[2] This is traced to the structure and bonding curiosities of such σ-dominant carbene moiety[3] on the electron-rich and soft late-metals that usually require a balance of σ and π ligands. Much of the interest is also driven by the catalytic interest of gold.[4] Recent developments also suggested some unique catalytic[5] and biomedical[6] features of gold carbenes. To date, Au(I) NHC complexes[7] continue to emerge but their Au(III) analogues are still uncommon. Oxidative addition of Au(I) (d^{10}) to Au(III) (d^8) by halogen remains the preferred method for the likes of $AuCl_3(NSHC)$[8] (*N,S*-heterocyclic carbene), which was among the earliest Au(III) carbenes, $AuBr_3(NHC)$ complexes, which were crystallographically established[9], and, more recently, cationic $[AuI_2(NHC)_2]^+$[10] and $[Au_2Br_2(bis\text{-}NHC)_2]^{2+}$.[11] We have been studying the use of NSHC as an alternative to the more common NHC ligands in d^8 complexes.[12] In this paper, we present an alternative methodology for Au(III) carbene preparation by using an olefin-in-proximity provided by an allyl *N*-substituent of the carbene to capture the halogen for concomitant olefin bromination and gold oxidation. This generates in a single step a cyclometallated Au(III) NSHC complex and exemplifies the use of an allyl functionalised NSHC carbene ligand.[13]

Results and discussion

Attempts to prepare a stable Au(I) NSHC complex from the reaction between AuCl(tht) (tht = tetrahydrothiophene) and *N*-3-propenylbenzothiazolium bromide in the presence of NaO^tBu or KO^tBu could not give any isolatable and identifiable product. However, metathesis reaction of AuCl(tht) with $LiN(SiMe_3)_2$ gives $[Au\{N(SiMe_3)_2\}(tht)]$, which further reacts with *N*-3-propenylbenzothiazolium bromide to yield AuBr(NSHC) (NSHC = *N*-allylbenzothiazolin-2-ylidene) (**1**).

Oxidation of **1** by excess iodine in CH_2Cl_2 gives the expected Au(III) but complicated by ligand migration, bromide dissociation and iodination to give the bis-carbene complex $[AuI_2(NSHC)_2]^+I_3^-$ (**2**), the NHC form of the cation has been reported earlier[10] (Scheme 1). The formation of a triiodide salt from addition of iodine to iodide has also been observed in similar cationic Pd-NSHC carbene complexes.[12a] The byproduct $AuBr_2(C_6H_4SCNCH_2CHCH_2Br)$ (**3**) was unexpected as there was no external or additional source of bromine or bromide. It probably arises from oxidation of **1** by adventitious Br_2 (generated from bromide oxidation in **1**). Complex **3** can be prepared in higher yield directly from the oxidation of **1** with Br_2 (Scheme 1). It probably occurs *via* a pathway similar to the ionic mechanism known for halogen addition to olefin (Scheme 2). Similar cyclometalated reactions have been reported in the bromination of Au(I), but not Pd(II), with olefinic tertiary phosphines.[14] To the best of our knowledge, this is the first cyclometalated product of Au(III) carbene. The ESI-MS mass spectrometric data of **2** support a dibiscarbene moiety ($[AuI_2(NSHC)_2]^+$ $m/z = 800.7$).



Scheme 1 Synthesis of Au(III) NSHC complexes from halogenation of **1**.

The crotyl (but-2-en-1-yl) derivative of **1**, *viz.* AuBr(NSHC) (NSHC = *N*-crotylbenzothiazolin-2-ylidene) (**4**) has been prepared for comparison. Bromination of **4** does not lead to

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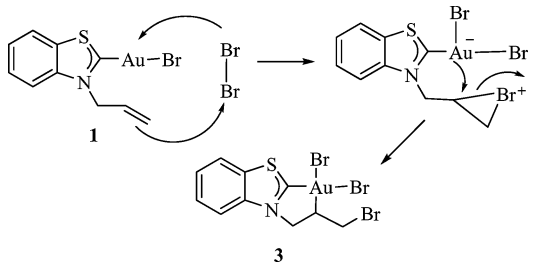
† CCDC reference numbers 732077–732079 and 739702. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b909661b



Scheme 2 Proposal mechanism of cyclometallation in **3**.

cyclometallation under similar conditions. An X-ray analysis of the product reveals a straightforward oxidative addition at the metal to give $AuBr_3(C_6H_4SCNCH_2CH{=}CHCH_3)$ (**5**). Experiments on related complexes with other alkenyl substituents are ongoing.

Complexes **1–3** and **5** have been isolated and characterised by X-ray single-crystal diffraction analysis. Complex **1** (Fig. 1) is a d^{10} complex with linear Au(I). The Au(1)–C(1) bond (1.989(7) Å) is comparable to those in other AuBr(NHC) complexes such as (IPr)–AuBr (1.975(5) Å).[9] The allyl olefin group (C(9)–C(10) 1.32(1) Å), which maintains its π character, is twisted away from the metal to avoid non-bonding interactions. Complexes **2**, **3** and **5** (Fig. 2–4) are d^8 Au(III) with a typical sq planar geometry. Complex **2** has two mutually-*trans* carbenes with relatively long Au-bonds [Au(1)–C(1) 2.04(1) Å] presumably weakened by the high *trans* influence of the carbene ligand. Complex **3** is most intriguing with two types of Au–C bonds, namely, the shorter Au–C(carbene) (1.97(1) Å) and longer Au–C(alkyl) (2.11(1) Å), within a cyclometallated 5-membered ring. Their difference in *trans* influence leads to two *trans* Au–Br bonds of significantly different lengths (2.469(1) and 2.547(1) Å). The shorter Au–Br bond is *trans* to the carbene, suggesting that the alkyl CH exerts a stronger *trans* influence than the NSHC carbene. The crotyl substituent of **5** is twisted away from the metal such that there is negligible interaction between the pendant olefin and the gold center; this could offer a possible explanation on the absence of proximity effect that could drive cyclometallation. Its Au–carbene bond (Au(1)–C(1) 2.02(1) Å) is longer than that in **3**, indicating the strength inherent of a chelate in the latter. This weaker Au–C bond in **5**, together with the absence of cyclometallation, leads to

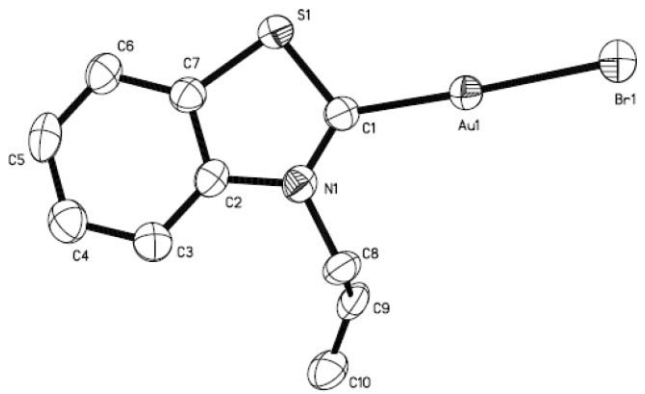


Fig. 1 ORTEP diagram of complex **1** with 30% thermal ellipsoids and labeling scheme; hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)–C(1) 1.989(7), Au(1)–Br(1) 2.3790(8), C(9)–C(10) 1.32(1), C(1)–Au(1)–Br(1) 177.1(2), C(10)–C(9)–C(8) 124.8(7).

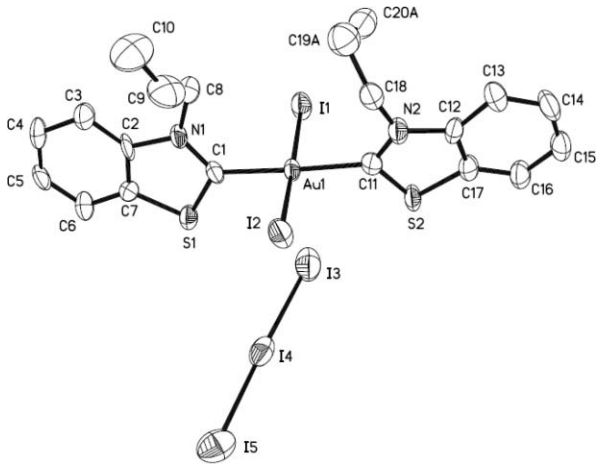


Fig. 2 ORTEP diagram of complex **2** with 30% thermal ellipsoids and labeling scheme; hydrogen atoms and solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)–C(1) 2.04(1), Au(1)–C(11) 2.05(1), Au(1)–I(1) 2.614(1), Au(1)–I(2) 2.614(1), C(9)–C(10) 1.33(3), C(19A)–C(20A) 1.32(1), C(1)–Au(1)–C(11) 176.4(5), C(1)–Au(1)–I(2) 92.2(4), C(1)–Au(1)–I(1) 88.1(4), C(11)–Au(1)–I(2) 91.3(3), C(11)–Au(1)–I(1) 88.4(3), I(2)–Au(1)–I(1) 174.76(4), I(5)–I(4)–I(3) 177.90(5).

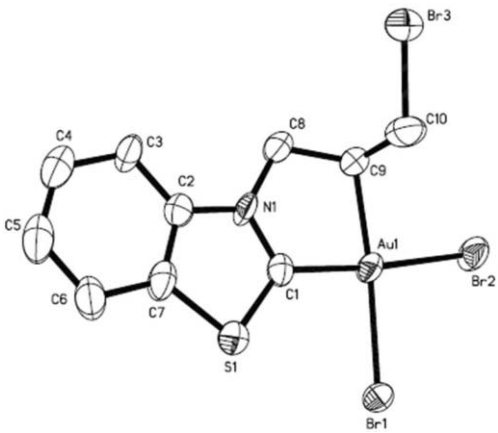


Fig. 3 ORTEP diagram of complex **3** with 30% thermal ellipsoids and labeling scheme; hydrogen atoms and solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)–C(1) 1.97(1), Au(1)–C(9) 2.11(1), Au(1)–Br(1) 2.547(1), Au(1)–Br(2) 2.469(1), C(9)–C(10) 1.49(2), C(1)–Au(1)–C(9) 82.1(5), C(1)–Au(1)–Br(2) 174.7(3), C(9)–Au(1)–Br(2) 92.6(4), C(1)–Au(1)–Br(1) 91.5(3), C(9)–Au(1)–Br(1) 173.4(4), Br(2)–Au(1)–Br(1) 93.79(4), C(10)–C(9)–C(8) 113.5(1).

an overall shortening, and presumably strengthening, of all Au–Br bonds (Au(1)–Br(1) 2.420(1), Au(1)–Br(2) 2.431(1), Au(1)–Br(3) 2.409(1) Å) compared to those of **3** (Au(1)–Br(1) 2.547(1), Au(1)–Br(2) 2.469(1) Å).

All these Au(III) complexes (**2–3** and **5**) are significantly more stable than the corresponding Au(I) complexes (**1** and **4**) which decompose slowly to colloidal gold even in a protected atmosphere. There is no evidence of decomposition of **3** through the known reductive elimination pathway. A preliminary study of the catalytic activities of **1** and **3** towards hydration of phenylacetylene suggested that the Au(III) complex is about two-fold more active

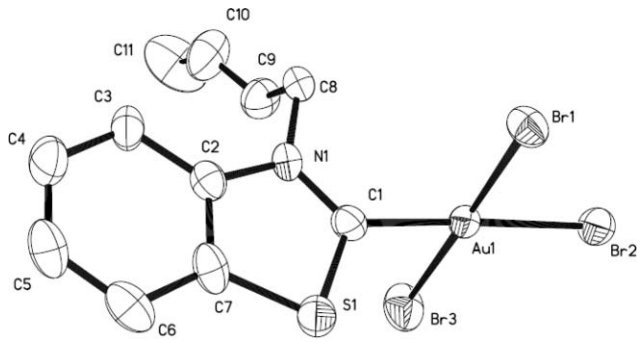


Fig. 4 ORTEP diagram of complex **5** with 30% thermal ellipsoids and labeling scheme; hydrogen atoms and solvent are omitted for clarity. Selected bond lengths (Å) and angles (°): Au(1)–C(1) 2.02(1), Au(1)–Br(1) 2.420(1), Au(1)–Br(2) 2.431(1), Au(1)–Br(3) 2.409(1), C(9)–C(10) 1.33(2), C(1)–Au(1)–Br(1) 87.9(3), C(1)–Au(1)–Br(2) 176.5(3), Br(1)–Au(1)–Br(2) 91.36(4), Br(1)–Au(1)–Br(3) 176.31(4), Br(2)–Au(1)–Br(3) 91.89(5), N(1)–C(1)–S(1) 113.0(7).

than Au(I), perhaps reflecting the instability of the latter. Details of these catalytic reactions will be reported in due course.

Conclusions

This study suggested that cyclometalated Au(III) heterocyclic carbenes can be conveniently prepared, isolated and are significantly more stable than their Au(I) heterocyclic carbene precursor. The conversion is achieved by a single-step allyl-assisted oxidation by halogen. The presence of two robust and *trans* directing Au–C bonds could provide a ready source of cyclometallated [Au(NHC)] moieties. Facile dissociation of the bromide(s) could also help to generate the vacant site needed for catalytic initiation.

Experimental

General procedures

All experiments were performed under a dry argon atmosphere using a Labmate glove box or by Schlenk techniques. THF and CH_2Cl_2 were distilled over benzophenone sodium-ketyl and CaH_2 respectively and kept under Ar. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX 500 spectrometers. ESI mass spectra were obtained using a Finnigan LCQ. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

Preparation of AuBr(NSHC) (NSHC = *N*-allylbenzothiazolin-2-ylidene) (1)

A solution of $LiN(SiMe_3)_2$ (34 mg, 0.2 mmol) in THF (2 mL) was added to a suspension of [AuCl(tht)] (64 mg, 0.2 mmol) in THF (2 mL). The mixture was stirred for 5 min, after which a suspension of *N*-allylbenzothiazolium bromide (45 mg, 0.18 mmol) in THF (3 mL) was added and stirred for 2 h. The resultant mixture was filtered through Celite. The solvent and $HN(SiMe_3)_2$ were removed under vacuum. The residual solid was dissolved in THF (1 mL) and left at low temperature (–30 °C) to afford white precipitate of **1**. Yield: 45 mg (0.1 mmol, 50%). ^{1}H NMR (500 MHz, THF-d_8): δ 8.17 (m, 1H, Ar-H), 8.08 (d, 1H, J = 8.2 Hz, Ar-H), 7.75–7.67 (m, 2H, Ar-H), 6.22–6.16 (m, 1H, CH), 5.60–5.58 (m, 2H, CH_2), 5.36–5.32 (m, 2H, CH_2CHCH_2). ^{13}C NMR (125.77 MHz, THF-d_8), 142.4, 133.2, 131.0, 127.9, 126.2, 123.0, 118.9, 116.0, 57.4. C(NCS) cannot be detected under this condition. Anal. Calcd for **1**, $C_{10}H_9AuBrNS$: C, 26.57; H, 2.01; N, 3.10. Found: C, 26.78; H, 2.01; N, 3.11.

Preparation of $[AuI_2(NSHC)_2]^+I_3^-$ (2)

Iodine (50 mg, 0.2 mmol) was added to a suspension of AuBr(NSHC) **1** (30 mg, 0.066 mmol) in CH_2Cl_2 (2 mL) and the mixture stirred for 1 h at r.t. The solvent was removed by vacuum and the residual iodine removed by washing with hexane (2 mL). The residue was redissolved in CH_2Cl_2 (1 mL), the solution filtered through Celite, and allowed to stand at low temperature (–30 °C) to obtain crystals of **2** (red) and **3** (colorless). Yield of **2**: 10.2 mg (0.0086 mmol, 39%). ^{1}H NMR (500 MHz, CD_2Cl_2): 8.02 (d, 2H, J = 8.2 Hz, Ar-H), 7.90 (d, 2H, J = 8.8 Hz, Ar-H), 7.72–7.67 (m, 4H, Ar-H), 6.19 (br, 2H, CH), 5.54 (m, 4H, CH_2), 5.42 (d, 4H, J = 6.3 Hz, CH=CH_2). ^{13}C NMR (125.77 MHz, CD_2Cl_2): 142.4, 135.1, 128.7, 127.8, 127.4, 123.0, 116.0, 58.0. C(NCS) cannot be detected under this condition. Yield of **3**: 2.1 mg (0.003 mmol, 15%). MS (ESI, positive mode) m/z (%): 800.7 (80) $[M - I_3]^+$. Anal. Calcd for **2**, $C_{20}H_{18}AuI_5N_2S_2$: C, 20.32; H, 1.53; N, 2.37. Found: C, 17.32; H, 1.36; N, 2.00. The elemental analysis remained unsatisfactory despite repeated purification and analysis, possibly due to contamination by I_5^-.

Preparation of $AuBr_2(C_6H_4SCNCH_2CHCH_2Br)$ (3)

Bromine (20 mg, 0.12 mmol) was added to the suspension of AuBr(NSHC) **1** (30 mg, 0.066 mmol) in THF (2 mL) and the mixture stirred for 1 h at r.t. The residual bromine and THF was removed under vacuum. The residual solid was redissolved in THF (1 mL) and the solution filtered through Celite and kept at low temperature (–30 °C) to obtain **3**. Yield: 33 mg (0.054 mmol, 81%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.39 (d, 1H, J = 7.6 Hz, Ar-H), 8.30 (d, 1H, J = 8.1 Hz, Ar-H), 7.84–7.76 (m, 2H, Ar-H), 5.03 (m, 1H, CH_2), 4.75 (m, 1H, CH_2), 4.42–4.28 (m, 3H), ^{13}C NMR (125.77 MHz, DMSO-d_6): δ 186.8 (NCS), 141.3, 133.4, 129.4, 127.9, 124.9, 118.3, 59.0, 57.9. Anal. Calcd for **3**·0.5THF, $C_{12}H_{13}AuBr_3O_{0.5}NS$: C, 22.24; H, 2.02; N, 2.16. Found: C, 22.79; H, 2.15; N, 2.12.

Preparation of AuBr(NSHC) (NSHC = *N*-crotylbenzothiazolin-2-ylidene) (4)

Compound **4** was prepared and purified using a method similar to that of **1**. Yield: 62%. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.26 (d, 1H, J = 8.2 Hz, Ar-H), 8.17 (d, 1H, J = 8.2 Hz, Ar-H), 7.76–7.68 (m, 2H, Ar-H), 5.88 (m, 1H, CH), 5.79 (m, 1H, CH), 5.40 (d, 2H, J = 5.6 Hz, CH_2), 1.66 (d, 3H, J = 6.3 Hz, CH_3). ^{13}C NMR (125.77 MHz, DMSO-d_6), 202.1 (NCS), 142.4, 133.2, 132.0, 128.7, 127.0, 124.5, 124.0, 116.8, 57.1, 17.89. Anal. Calcd for **4**·0.2THF, $C_{11.8}H_{12.6}AuBrO_{0.2}NS$: C, 29.49; H, 2.64; N, 2.91. Found: C, 29.66; H, 2.41; N, 3.15.

Preparation of $AuBr_3(C_6H_4SCNCH_2CH{=}CHCH_3)$ (5)

Compound **5** was prepared from Br_2 and **4** using a procedure similar to that of **3**. Yield: 65%. ^{1}H NMR (500 MHz, DMSO-d_6):

Table 1 Selected crystallographic data of complexes **1-3** and **5**

	1	**2**·CH_2Cl_2	**3**·CH_2Cl_2	**5**·0.25THF
Formula	$C_{10}H_9AuBrNS$	$C_{21}H_{20}AuCl_2I_5N_2S_2$	$C_{11}H_{11}AuBr_3Cl_2NS$	$C_{12}H_{13}AuBr_3NO_{0.25}S$
fw	452.12	1266.88	696.86	647.99
crystal system	Triclinic	Triclinic	Triclinic	Triclinic
space group	*P*-1	*P*-1	*P*-1	*P*-1
a/Å	7.9989(6)	11.1192(9)	7.8579(11)	8.9850(16)
b/Å	8.0038(6)	11.3298(9)	10.8044(15)	9.9425(18)
c/Å	9.5214(7)	13.0049(10)	11.3771(15)	11.506(2)
α/deg	92.4370(10)	86.981(2)	64.654(2)	109.135(3)
β/deg	94.8290(10)	74.880(2)	78.777(3)	99.547(4)
γ/deg	112.4620(10)	82.729(2)	87.187(3)	101.778(4)
V/Å^3	559.48(7)	1568.6(2)	855.6(2)	920.0(3)
Z	2	2	2	2
Dc/g cm^{-3}	2.684	2.682	2.705	2.339
μ/mm^{-1}	16.863	9.928	16.022	14.612
F(000)	412	1140	636	592
No of reflections collected	7173	11094	5904	6324
No of unique reflections	2573	7120	3901	4184
No. of observed reflections	2374	5277	3235	3072
θ range [deg]	2.15–27.49	1.62–27.48	2.02–27.50	2.26–27.48
R(int)	0.0391	0.0349	0.0373	0.0220
Parameters	127	317	191	200
T/K	223(2)	293(2)	293(2)	295(2)
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0331	0.0678	0.0674	0.0468
w$R_2{}^b$ [$I > 2\sigma(I)$]	0.0846	0.1788	0.1667	0.1319
$R_1{}^a$ (all data)	0.0363	0.0899	0.0794	0.0705
w$R_2{}^b$ (all data)	0.0860	0.1934	0.1739	0.1566
GOF^c	1.066	1.043	1.074	1.038
$\Delta\rho_{max}$/e Å^{-3}	2.143	4.543	5.358	1.805
$\Delta\rho_{min}$/e Å^{-3}	–1.192	–2.879	–3.762	–0.946

^{a} $R_1 = \sum\|F_0| - |F_c\|/\sum|F_0|$. ^{b} $wR_2 = \{w\sum(|F_0| - |F_c|)^2/\sum w|F_0|^2\}^{1/2}$. ^{c} GOF $= \{\sum w(|F_0| - |F_c|)^2/(n-p)\}^{1/2}$, where *n* is the number of reflections and *p* is the total number of parameters refined.

δ 8.40–8.34 (m, 2H, Ar-H), 7.85–7.78 (m, 2H, Ar-H), 5.19 (m, 1H, CH), 5.06–4.92 (m, 2H, CH_2), 4.48 (m, 1H, $CHCH_3$), 1.87 (d, 3H, J = 6.9 Hz, CH_3), ^{13}C NMR (125.77 MHz, DMSO-d_6): δ 187.9 (NCS), 141.0, 133.4, 129.5, 128.0, 125.1, 118.3, 64.8, 26.4. Anal. Calcd for **5**·0.6THF, $C_{13.4}H_{15.8}AuBr_3O_{0.6}NS$: C, 24.05; H, 2.38; N, 2.09. Found: C, 24.21; H, 2.24; N, 2.29.

X-Ray diffraction studies

The crystals were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector, using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects with the SMART suite programs and for absorption effects with SADABS. Structure solution and refinement were carried out with the SHELXTL suite of programs.[15] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Select crystal data for complexes **1-3** and **5** are summarized in Table 1.

Acknowledgements

We are grateful to the Agency of Science, Technology & Research (R143-000-364-305), Ministry of Education (R143-000-361-112) and the National University of Singapore for financial support and the reviewers for some useful comments. We thank G. K. Tan and S. W. Chien for their assistantance in X-ray analysis and monograph preparation respectively.

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