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Cycloaurated gold(III) complexes with monoanionic thiourea ligands

Tiffany S. Smith, William Henderson *, Brian K. Nicholson

Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand

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ABSTRACT

Using a simple one-pot procedure, reaction of cycloaurated gold(III) dihalide complexes [$LAuCl_2$] (L = 2-benzylpyridyl, 2-anilinopyridyl) with trisubstituted thioureas $PhNHC(S)NR_2$ (R = Me, Cy) and Me_3N in methanol, followed by addition of excess $NaBPh_4$ gave the salts $[LAu\{SC(=NR_2)NPh\}]^+BPh_4^-$ containing *N*,*S*-chelated thiourea monoanion ligands. The compounds were obtained in good yields, and were characterised by ESI MS, elemental microanalysis and in two cases by X-ray structure determinations. The series of complexes was extended by additional microscale reactions of $LAuCl_2$ complexes (L = 2-benzylpyridyl, 2-anilinopyridyl, 2-benzoylpyridyl or picolinamide) with a wide range of trisubstituted thioureas, with products identified by ESI MS.

1. Introduction

Thioureas are an interesting and easily synthesised class of ligand, which coordinate to metal centres in a variety of ways, as neutral, monoanionic or dianionic ligands, in monodentate or chelating modes [1,2]. In previous studies we have investigated the coordination chemistry of deprotonated trisubstituted thioureas $R^1NHC(S)NR^2R^3$, which can bind either as *N*,*S*-chelating ligands to rhodium(III) and ruthenium(II) [3], platinum(II) [4] and nickel(II) [5] or as monodentate ligands bonded through sulfur to gold(I) [6].

In this paper, we describe investigations into the synthesis and characterisation of analogous gold(III) complexes containing deprotonated trisubstituted thiourea ligands. The chemistry of gold with thiourea itself [$H_2NC(S)NH_2$] has been extensively investigated since thiourea provides an alternative lixiviant to cyanide for gold extraction from ores [7–9]. Unlike the well-established coordination chemistry of gold(I) towards thioureas and related ligands [10–13], the coordination chemistry of gold(III) towards thioureas is rather limited. Trisubstituted *N*,*N*-dialkyl-*N*′-aroylthioureas have been found to extract gold(III) into an organic phase, though the nature of the extracted gold(III) species was not determined [14]. A previous investigation into the reactions of cycloaurated gold(III) complexes with MeNHC(S)NHMe and Ag_2O in refluxing dichloromethane did not give a gold(III)-thiourea complex, in contrast to the analogous chemistry with platinum(II), instead giving multimetallic gold–silver–sulfide–halide aggregates from thiourea desulfurisation [15]. Gold(III) complexes containing cyclometallated *N*,*C*-donor ligands have been attracting recent interest because of their relationship to isoelectronic platinum(II) complexes and hence potential anticancer activity [16]. Reaction of the cycloaurated complex (2-anp)$AuCl_2$ **1a** with the related thiosemicarbazone $Ph_2NNHC(S)NHPh$ and Et_3N in methanol gave the five-membered ring chelate complex **2** [17] while reaction of $(C_6H_4CH_2NMe_2)AuCl_2$ with various thiosemicarbazone and nitrogen-containing heterocyclic thiol ligands has been described [18–22]. However complexes containing chelating thiourea ligands have not been reported.

2. Results and discussion

The reactions of the cycloaurated gold(III) chloride complexes derived from 2-anilinopyridine, (2-anp)$AuCl_2$ **1a** or 2-benzylpyridine, (2-bp)$AuCl_2$ **1b**, with one mole equivalent of the thioureas $PhNHC(S)NCy_2$ or $PhNHC(S)NMe_2$ in methanol in the presence of Me_3N base results in clear yellow solutions, from which the product BPh_4^- salts **3a**–**c** can be isolated by addition of excess $NaBPh_4$, Scheme 1 . The complexes (after filtration, washing and drying) were isolated as yellow solids, readily soluble in dichloromethane and chloroform, but poorly soluble in alcohols and water. Over a prolonged period of storage at room temperature, the complexes show considerable darkening, but are stable for many months at −18 °C. The ESI mass spectra of the isolated complexes **3a**–**c** show a single dominant parent cation as expected (data are summarised in Table 1), though in some cases weak ions due to the bis(cycloaurated) complexes **4** were also observed at *m*/*z* 535 (anilinopyridyl) or 533 (benzylpyridyl). The complexes were also characterised by NMR spectroscopy and microelemental analysis, with all three complexes giving satisfactory agreement between

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* Corresponding author. Tel.: +64 7 838 4656.
E-mail address: w.henderson@waikato.ac.nz (W. Henderson).

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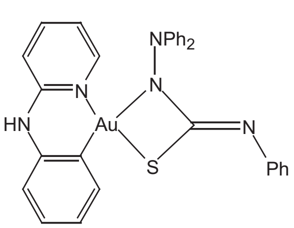

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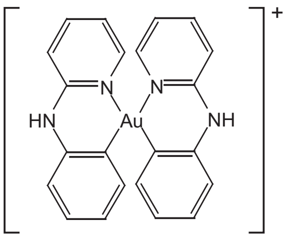

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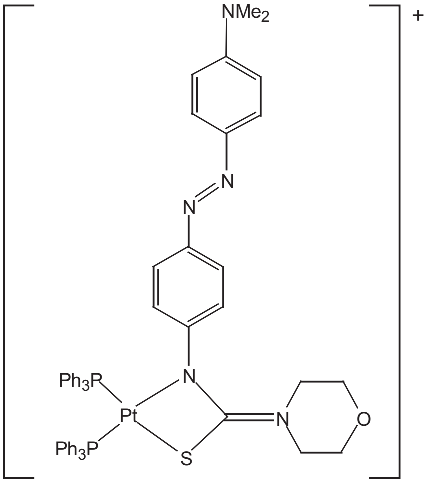

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Table 1
Cationic gold(III) thiourea complexes $[LAu\{SC(NR^2R^3)NR^1\}]^+$ **3** prepared in this work from the thioureas $R^1NHC(S)NR^2R^3$, together with their ESI MS data (L = cycloaurated ligand).

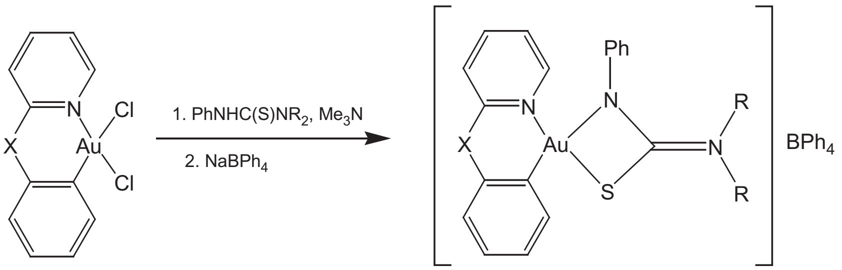
Complex **3**	Ligand	$R^1NHC(S)NR^1R^2$			$[M]^+$ ESI MS *m/z*	
		R^1	R^2	R^3	Obs.	Calc.
Isolated products						
a	2-anp	Ph	Cy	Cy	681.13	681.23
b	2-anp	Ph	Me	Me	545.03	545.11
c	2-bp	Ph	Me	Me	544.03	544.11
d	2-anp	Ph	$(CH_2CH_2)_2O$		587.02	587.12
Microscale syntheses						
e	2-bp	Ph	Bz	Bz	696.13	696.17
f	2-bp	Ph	Cy	Cy	680.15	680.24
g	2-bp	Ph	$(CH_2CH_2)_2O$		586.04	586.12
h	2-bp	$CH_2{=}CHCH_2$	Bz	Bz	660.14	660.17
i	2-bp	Ph	$(CH_2)_4$		570.06	570.13
j	2-bp	Ph	$(CH_2)_5$		584.08	584.14
k	2-bp	Ph	$(CH_2CH_2)_2S$		602.07	602.10
l	2-bp	Ph	Me	CH_2An	720.10	720.17
m	2-bp	$p\text{-}NO_2C_6H_4$	$(CH_2CH_2)_2O$		631.04	631.11
n	2-bp	$p\text{-}NO_2C_6H_4$	Me	Me	589.03	589.10
o	2-bzp	Ph	Me	Me	558.03	558.09
p	pla	Ph	Me	Me	497.01	497.07

Abbreviations: 2-anp, 2-anilinopyridyl; 2-bp, 2-benzylpyridyl; 2-bzp, 2-benzoylpyridyl; pla, picolinamide; Bz, CH_2Ph; An, 9-anthracenyl; Cy, cyclohexyl.

observed and calculated values. Complexes **3a** and **3b**, containing the anilinopyridyl ligand, showed a singlet peak in the region 10.7–10.8 ppm in their ^1H spectra due to the NH proton, confirmed by COSY and HSQC spectra which were devoid of a correlation between this proton and other protons or a carbon atom, respectively.

In some preparations of these and analogous complexes, yields were apparently greater than 100%, the resulting solids gave C, H and N percentages that differed markedly from theoretical values (even after extensive drying), and NMR spectra showed substantially more intense aryl resonances, arising from additional BPh_4^-. A singlet was also observed at δ 2.8 in the ^1H NMR, assigned to the methyl protons of a Me_3N moiety (presumably Me_3NH^+). This was supported by elemental analysis on a sample of the complex $[(2\text{-anp})Au\{SC(NMe_2)N(C_2H_4)_2O\}]BPh_4$ **3d** (Table 1, prepared according to the procedure described in the Experimental section), which gave good agreement between the experimentally determined percentages of C, H and N with those calculated for **3d**·BPh_4 co-crystallised with 0.5 mol equivalents of $(Me_3NH)BPh_4$. Although we have used trimethylamine and $NaBPh_4$ in the successful synthesis of other BPh_4^- salts in good purity, e.g., platinum(II) complexes of thiourea monoanions [4], on one previous occasion (hydrogen-bonded) adducts of a platinum(II) thiosalicylate complex with $(Me_3NH)BPh_4$ were obtained [23].

In order to unambiguously characterise the complexes, X-ray structure determinations were carried out on $[(2\text{-anp})Au\{SC(NCy_2)NPh\}]BPh_4$ **3a** and $[(2\text{-anp})Au\{SC(NMe_2)NPh\}]BPh_4$ **3b**. The structures of the cations are shown in Figs. 1 and 2, respectively, while selected bond lengths and angles are given in Table 2. They confirm the expected formulation of the compounds as cycloaurated anilinopyridylgold(III) cations containing thiourea monoanion ligands, together with a BPh_4^- counteranion. The thiourea ligand is coordinated to gold through the NPh and S donors,



3a X = NH, R = Cy
3b X = NH, R = Me
3c X = CH_2, R = Me
3d X = NH, RR = $(CH_2CH_2)_2O$

Scheme 1. Synthesis of the isolated cycloaurated gold(III) trisubstituted thiourea complexes **3a–c**.