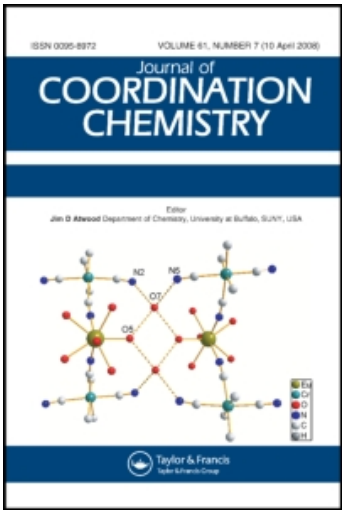

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Microwave methods for the synthesis of gold(III) complexes

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First published on: 05 October 2010

Journal of Coordination Chemistry
Vol. 64, No. 1, 10 January 2011, 38–47

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Microwave methods for the synthesis of gold(III) complexes

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(*Received 9 June 2010; in final form 2 August 2010*)

New microwave methods were developed for the synthesis of cationic and neutral gold(III) complexes. Six examples of $[AuCl_2(N–N)][PF_6]$, containing 2,2′-bipyridine-type ligands, and three examples of $AuCl_2(C–N)$, containing cyclometallated 2-phenylpyridine-type ligands, were successfully prepared. Two of the complexes, $[AuCl_2$(5,5′-dimethyl-2,2′-bipyridine)$][PF_6]$ and $[AuCl_2$(4,4′,5,5′-tetramethyl-2,2′-bipyridine)$][PF_6]$, have not been previously reported. Generally, the microwave-heated reactions gave analytically pure products within minutes – a substantial improvement over conventional procedures. In conjunction, the thermal stabilities of some of the complexes were studied by thermogravimetric analysis. The transformation of $AuCl_3$(2-(*p*-tolyl)pyridine) into its cyclometallated analog $AuCl_2$(tpy), marked by the loss of a mass corresponding to HCl, was observed.

Keywords: Gold; Coordination complex; Cyclometallation; Microwave; Synthesis

1. Introduction

Interest in the coordination, organometallic, and biological chemistry of gold continues to grow. Gold(III) complexes are being investigated as catalysts for organic transformations [1], and also as potential anti-cancer drugs [2, 3]. They may prove to be suitable catalysts for selective oxidation-functionalization of hydrocarbons [4–6]. Yet, despite such wide-ranging interest in gold(III) complexes, the synthetic methods available for preparing them are, in many cases, underdeveloped.

While microwave heating has become ubiquitous in organic chemistry [7], it has not yet been fully embraced by the organometallic/inorganic community. Microwave heating has been employed with much success in transition metal-catalyzed synthesis of organic compounds [8]. However, there are still relatively few reports of microwave-heated syntheses of *transition metal complexes* [9, 10]. Even so, it is already apparent that synthetic inorganic and organometallic chemistry have much to benefit from microwave technology.

The main advantage that microwave heating provides is the ability to *rapidly* heat reaction mixtures to high temperatures. Thermal effects peculiar to microwave heating

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ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.521818

may also be beneficial. These include inverted heat transfer (heating from the inside out), inhomogeneity in the electromagnetic field (producing hot spots), and the selective heating of polar molecules [11]. The role of non-thermal effects, such as stabilization of polar transition states in the presence of microwave radiation, is still controversial [12, 13].

In the context of our ongoing investigations of C–H activation [14–16], and our recent focus on gold in this respect [17, 18], we report here improved microwave methods for the synthesis of gold(III) complexes. We have investigated two classes of gold(III) complexes: cationic complexes bearing 2,2′-bipyridine-type ligands, and, inspired by the work of Ghedini and co-workers [10], neutral complexes containing cyclometallated C–N ligands such as 2-phenylpyridine. We have found that microwave heating provides *substantial* benefits to the syntheses of both types. We have also examined the thermal stabilities of some of these gold complexes, an inquiry germane to some of our high-temperature microwave syntheses.

2. Experimental

2.1. *General comments*

The compounds 4,4′,5,5′-tetramethyl-2,2′-bipyridine [19, 20], **1a** [21], **1b** [22], **1c** [23], **1d** [23], **1e** [24], $AuCl_3$(2-phenylpyridine) [25], $AuCl_3$(2-(*p*-tolyl)pyridine) [26], $AuCl_3$(2-benzylpyridine) [27], $AuCl_3$(2-ethylpyridine) [28], **2a** [25, 29], **2b** [26], and **2c** [27], have been reported. Here we report the NMR spectra of **1a–1g** in CD_3CN, a solvent that we believe is the ideal for studying the reactivity of these complexes.

2.2. *Materials and methods*

Commercially available ligands, $HAuCl_4 \cdot 3H_2O$ (Sigma–Aldrich, Inc.), and deuterated solvents (Cambridge Isotope Laboratories, Inc.) were used as received. Microwave reactions, in sealed Teflon® vessels, were performed in a multi-mode Milestone MicroSYNTH oven equipped with magnetic stirring and temperature sensing/control. Elemental analyses were performed by Mikroanalytisches Laboratorium Kolbe, Mülheim an der Ruhr, Germany. NMR was performed with Bruker DPX200 and DPX300 spectrometers. Mass spectrometry was performed with Waters ProSpec (EI) and Q-TOF-2 (ESI) instruments. TGA were performed with a Rheometric Scientific STA 1500. The samples were heated at $10^{\circ}C\,min^{-1}$ in quartz crucibles under a flow of nitrogen.

2.3. *General method for [$AuCl_2$(N–N)][PF_6] (1a–1g)*

The ligand (1.0 mmol), $NaPF_6$ (3.0 mmol, 504 mg), $HAuCl_4 \cdot 3H_2O$ (1.0 mmol, 394 mg), CH_3CN, and water were combined. This mixture was heated in a sealed vessel in the microwave oven. After cooling, the product was collected on a fine frit and washed with 2×5 mL of water, 5 mL of Et_2O, and dried under a stream of air for 30 min.

2.3.1. [$AuCl_2$(2,2′-bipyridine)][PF_6] (1a). This synthesis used 5 mL of CH_3CN and 25 mL of water. The reaction mixture was heated at 110°C for 10 min. While still warm, the vessel was placed in a cold water bath for 60 min. The product was obtained in 96% yield. ^{1}H NMR (200 MHz, CD_3CN): δ 8.06 (td, 5,5′-C*H*, $J_1 = 6.2$ Hz, $J_2 = 2.8$ Hz, 2H), 8.57 (m, 3,3′ and 4,4′-C*H*, 4H), 9.45 (d, 6,6′-C*H*, $J = 6.3$ Hz, 2H). $^{31}P\{^1H\}$ NMR (81 MHz, CD_3CN): $\delta -144$ (septet, PF_6^-, $J_{F-P} = 707$ Hz). TOF ESI(+) MS (CH_3CN): $m/z = 423$ $[AuCl_2(N–N)]^+$. TOF ESI(−) MS (CH_3CN): $-m/z = 145$ $[PF_6]^-$. Anal. Calcd for $C_{10}H_8AuCl_2F_6N_2P$ (%): C, 21.11; H, 1.42; N, 4.92. Found (%): C, 20.97; H, 1.55; N, 4.87.

2.3.2. [$AuCl_2$(1,10-phenanthroline)][PF_6] (1b). This synthesis used 10 mL of CH_3CN and 20 mL of water. The reaction mixture was heated at 110°C for 10 min. While still warm, the vessel was placed in a cold water bath for 60 min. The product was obtained in 93% yield. ^{1}H NMR (200 MHz, CD_3CN): δ 8.34 (dd, 3,8-C*H*, $J_1 = 8.3$ Hz, $J_2 = 5.8$ Hz, 2H), 8.40 (s, 5,6-C*H*, 2H), 9.17 (d, 4,7-C*H*, $J = 7.7$ Hz, 2H), 9.69 (d, 2,9-C*H*, $J = 5.7$ Hz, 2H). $^{31}P\{^1H\}$ NMR (81 MHz, CD_3CN): $\delta -144$ (septet, PF_6^-, $J_{F-P} = 707$ Hz). TOF ESI(+) MS (CH_3CN): $m/z = 447$ $[AuCl_2(N–N)]^+$. TOF ESI(−) MS (CH_3CN): $-m/z = 145$ $[PF_6]^-$. Anal. Calcd for $C_{12}H_8AuCl_2F_6N_2P$ (%): C, 24.30; H, 1.36; N, 4.72. Found (%): C, 24.17; H, 1.53; N, 4.69.

2.3.3. [$AuCl_2$(4,4′-dimethyl-2,2′-bipyridine)][PF_6] (1c). This synthesis used 5 mL of CH_3CN and 25 mL of water. The reaction mixture was heated at 120°C for 20 min. While still warm, the vessel was placed in ice for 30 min. The product was obtained in 99% yield. ^{1}H NMR (200 MHz, CD_3CN): δ 2.68 (s, CH_3, 6H), 7.84 (d, 5,5′-C*H*, $J = 6.2$ Hz, 2H), 8.39 (s, 3,3′-C*H*, 2H), 9.23 (d, 6,6′-C*H*, $J = 6.3$ Hz, 2H). $^{31}P\{^1H\}$ NMR (81 MHz, CD_3CN): $\delta -144$ (septet, PF_6^-, $J_{F-P} = 707$ Hz). TOF ESI(+) MS (CH_3CN): $m/z = 451$ $[AuCl_2(N–N)]^+$. TOF ESI(−) MS (CH_3CN): $-m/z = 145$ $[PF_6]^-$. Anal. Calcd for $C_{12}H_{12}AuCl_2F_6N_2P$ (%): C, 24.14; H, 2.03; N, 4.69. Found (%): C, 24.13; H, 2.21; N, 4.64.

2.3.4. [$AuCl_2$(4,4′-dimethoxy-2,2′-bipyridine)][PF_6] (1d). This synthesis used 10 mL of CH_3CN and 20 mL of water. The reaction mixture was heated at 120°C for 20 min. While still warm, the vessel was placed in ice for 30 min. The product was obtained in 93% yield. ^{1}H NMR (200 MHz, CD_3CN): δ 4.17 (s, CH_3, 6H), 7.43 (dd, 5,5′-C*H*, $J_1 = 7.1$ Hz, $J_2 = 2.9$ Hz, 2H), 7.99 (d, 3,3′-C*H*, $J = 2.9$ Hz, 2H), 9.17 (d, 6,6′-C*H*, $J = 7.2$ Hz, 2H). $^{31}P\{^1H\}$ NMR (81 MHz, CD_3CN): $\delta -144$ (septet, PF_6^-, $J_{F-P} = 707$ Hz). TOF ESI(+) MS (CH_3CN): $m/z = 483$ $[AuCl_2(N–N)]^+$. TOF ESI(−) MS (CH_3CN): $-m/z = 145$ $[PF_6]^-$. Anal. Calcd for $C_{12}H_{12}AuCl_2F_6N_2O_2P$ (%): C, 22.91; H, 1.92; N, 4.45. Found (%): C, 22.70; H, 2.12; N, 4.33.

2.3.5. [$AuCl_2$(4,4′-di-*t*-butyl-2,2′-bipyridine)][PF_6] (1e). This synthesis used 10 mL of CH_3CN and 20 mL of water. The reaction mixture was heated at 120°C for 20 min. While still warm, the vessel was placed in ice for 30 min. The identity of the product (576 mg) was confirmed by ^{1}H and ^{31}P NMR and TOF ESI (+ and −) MS. However, elemental analysis indicated that it was impure, probably due to the presence of some

metallic gold. Anal. Calcd for $C_{18}H_{24}AuCl_2F_6N_2P$ (%): C, 31.74; H, 3.55; N, 4.11. Found (%): C, 29.77; H, 3.38; N, 3.79.

2.3.6. [$AuCl_2$(5,5′-dimethyl-2,2′-bipyridine)][PF_6] (1f). This synthesis used 5 mL of CH_3CN and 25 mL of water. The reaction mixture was heated at 120°C for 20 min. While still warm, the vessel was placed in ice for 30 min. The product was obtained in 97% yield. ^{1}H NMR (200 MHz, CD_3CN): δ 2.61 (s, C*H*$_3$, 6H), 8.38 (s, 3,3′ and 4,4′-C*H*, 4H), 9.20 (s, 6,6′-C*H*, 2H). ^{31}P{^{1}H} NMR (81 MHz, CD_3CN): $\delta -144$ (septet, PF_6^-, $J_{F-P} = 707$ Hz). TOF ESI(+) MS (CH_3CN): $m/z = 451$ [$AuCl_2$(N–N)]$^+$. TOF ESI(−) MS (CH_3CN): $-m/z = 145$ [PF_6]$^-$. Anal. Calcd for $C_{12}H_{12}AuCl_2F_6N_2P$ (%): C, 24.14; H, 2.03; N, 4.69. Found (%): C, 24.12; H, 2.12; N, 4.54.

2.3.7. [$AuCl_2$(4,4′,5,5′-tetramethyl-2,2′-bipyridine)][PF_6] (1g). This synthesis used 5 mL of CH_3CN and 25 mL of water. The reaction mixture was heated at 120°C for 20 min. While still warm, the vessel was placed in a cold water bath for 60 min. The product was obtained in 94% yield. ^{1}H NMR (200 MHz, CD_3CN): δ 2.50 (s, C*H*$_3$, 6H), 2.58 (s, C*H*$_3$, 6H), 8.29 (s, 3,3′-C*H*, 2H), 9.02 (s, 6,6′-C*H*, 2H). ^{31}P{^{1}H} NMR (81 MHz, CD_3CN): $\delta -144$ (septet, PF_6^-, $J_{F-P} = 707$ Hz). TOF ESI(+) MS (CH_3CN): $m/z = 479$ [$AuCl_2$(N–N)]$^+$. TOF ESI(−) MS (CH_3CN): $-m/z = 145$ [PF_6]$^-$. Anal. Calcd for $C_{14}H_{16}AuCl_2F_6N_2P$ (%): C, 26.90; H, 2.58; N, 4.48. Found (%): C, 27.07; H, 2.33; N, 4.54.

2.4. *General method A for $AuCl_2$(C–N) (2a–2c)*

One millimole of $AuCl_3$(2-phenylpyridine), $AuCl_3$(2-(*p*-tolyl)pyridine), or $AuCl_3$(2-benzylpyridine) was combined with 30 mL of water. This mixture was heated in a sealed vessel in the microwave oven. After cooling, the product was collected on a fine frit, washed with 3 × 5 mL of water, and dried under a stream of air for 60 min.

2.4.1. $AuCl_2$(ppy) (2a) by method A. The mixture was heated at 160°C for 60 min. The product was obtained in 94% yield. The ^{1}H NMR spectrum agreed with that reported in the literature [25]. Anal. Calcd for $C_{11}H_8AuCl_2N$ (%): C, 31.30; H, 1.91; N, 3.32. Found (%): C, 31.14; H, 1.72; N, 3.17.

2.4.2. $AuCl_2$(tpy) (2b) by method A. The mixture was heated at 160°C for 30 min. The product was obtained in 92% yield. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.40 (s, C*H*$_3$, 3H), 7.30 (d, 4′-C*H*, $J = 7.7$ Hz, 1H), 7.62 (s, 6′-C*H*, 1H), 7.68–7.75 (m, 5-C*H*, 1H), 7.85 (d, 3′-C*H*, $J = 7.9$ Hz, 1H), 8.32–8.39 (m, 3,4-C*H*, 2H), 9.49 (d, 6-C*H*, $J = 6.1$ Hz, 1H). Anal. Calcd for $C_{12}H_{10}AuCl_2N$ (%): C, 33.05; H, 2.31; N, 3.21. Found (%): C, 32.81; H, 2.31; N, 3.19.

2.4.3. $AuCl_2$(bnpy) (2c) by method A. The mixture was heated at 140°C for 20 min. The product was obtained in 93% yield. ^{1}H NMR (300 MHz, DMSO-d_6): δ 4.34 and 4.62 (AB pattern, C*H*$_2$, $J = 15.2$ Hz, 2H), 7.07 (t, Ar, $J = 7.5$ Hz, 1H), 7.14–7.28 (m, Ar, 2H), 7.41 (d, Ar, $J = 7.9$ Hz, 1H), 7.71 (t, 5-C*H*, $J = 6.8$ Hz, 1H), 7.99 (d, 3-C*H*,

$J = 7.6$ Hz, 1H), 8.26 (td, 4-C*H*, $J_1 = 7.7$ Hz, $J_2 = 1.3$ Hz, 1H), 9.17 (d, 6-C*H*, $J = 5.9$ Hz, 1H). Anal. Calcd for $C_{12}H_{10}AuCl_2N$ (%): C, 33.05; H, 2.31; N, 3.21. Found (%): C, 32.94; H, 2.67; N, 3.04.

2.5. *General method B for $AuCl_2$(C–N) (2a–2c)*

The ligand (1.0 mmol), $HAuCl_4 \cdot 3H_2O$ (1.0 mmol, 394 mg), and 30 mL of water were combined. This mixture was heated in a sealed vessel in the microwave oven. After cooling, the product was collected on a fine frit, washed with 3×5 mL of water, and dried under a stream of air for 60 min.

2.5.1. $AuCl_2$(ppy) (2a) by method B. The mixture was heated at 160°C for 60 min. The product was obtained in 83% yield. The ^{1}H NMR spectrum agreed with that reported in the literature [25]. Anal. Calcd for $C_{11}H_8AuCl_2N$ (%): C, 31.30; H, 1.91; N, 3.32. Found (%): C, 31.04; H, 1.81; N, 3.14.

2.5.2. $AuCl_2$(tpy) (2b) by method B. The mixture was heated at 160°C for 30 min. The product was obtained in 87% yield. The ^{1}H NMR spectrum was identical to that in Section 2.4.2. Anal. Calcd for $C_{12}H_{10}AuCl_2N$ (%): C, 33.05; H, 2.31; N, 3.21. Found (%): C, 32.53; H, 2.32; N, 3.18.

2.5.3. $AuCl_2$(bnpy) (2c) by method B. The mixture was heated at 160°C for 20 min. The product was obtained in 78% yield. The ^{1}H NMR spectrum was identical to that in Section 2.4.3. Anal. Calcd for $C_{12}H_{10}AuCl_2N$ (%): C, 33.05; H, 2.31; N, 3.21. Found (%): C, 32.97; H, 2.68; N, 2.84.

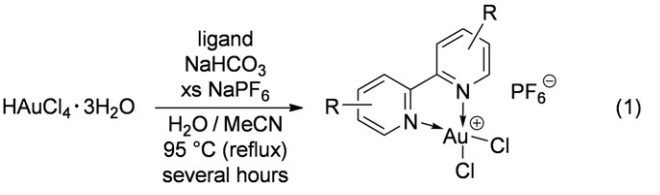
2.6. *[$AuCl_2$(4,4′-di-t-butyl-2,2′-bipyridine)][PF_6] (1e)*

The title compound was prepared by a method adapted from the literature [24]. $NaHCO_3$ (2.0 mmol, 0.17 g) and $HAuCl_4 \cdot 3H_2O$ (2.0 mmol, 0.79 g) were combined, dissolved in 70 mL of water, and stirred until CO_2 evolution ceased. CH_3CN (70 mL), $NaPF_6$ (6.0 mmol, 1.01 g), and 4,4′-di-*t*-butyl-2,2′-bipyridine (2.2 mmol, 0.59 g) were added. The mixture was refluxed for 3 h. The resulting translucent solution was placed in a cold water bath for 30 min and then in an ice-water bath for 30 min; a mass of yellow needles formed. The crystals were broken up by stirring, collected on a fine frit, and washed with 2×5 mL of aqueous $NaHCO_3$ (0.05 M), 2×10 mL of water, and 2×5 mL of Et_2O. The product was dried under a stream of air for 15 min and then under vacuum for 60 min, giving 1.06 g (1.56 mmol, 78% yield). ^{1}H NMR (200 MHz, CD_3CN): δ 1.50 (s, *t*-Bu, 18H), 8.00 (dd, 5,5′-C*H*, $J_1 = 6.6$ Hz, $J_2 = 2.3$ Hz, 2H), 8.52 (d, 3,3′-C*H*, $J = 2.2$ Hz, 2H), 9.29 (d, 6,6′-C*H*, $J = 6.5$ Hz, 2H). ^{31}P{^{1}H} NMR (81 MHz, CD_3CN): $\delta - 144$ (septet, PF_6^-, $J_{F-P} = 707$ Hz). TOF ESI(+) MS (CH_3CN): $m/z = 535$ $[AuCl_2(N–N)]^+$. TOF ESI(−) MS (CH_3CN): $-m/z = 145$ $[PF_6]^-$. Anal. Calcd for $C_{18}H_{24}AuCl_2F_6N_2P$ (%): C, 31.74; H, 3.55; N, 4.11. Found (%): C, 31.71; H, 3.49; N, 4.07.

3. Results and discussion

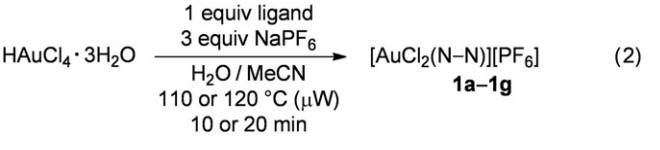
3.1. *[AuCl$_2$(N–N)][PF$_6$]*

Gold(III) 2,2′-bipyridine complexes have been known for over 70 years [30–32]. The chloro complex, [AuCl$_2$(2,2′-bipyridine)][Cl], was first reported by Block and Bailar [33], although it was impure. The pure compound and the analogous perchlorate salt were reported 8 years later by Harris and Lockyer [34]. More recently, the PF_6^- salts of $[AuCl_2(N–N)]^+$ (N–N = 2,2′-bipyridine and related) have been reported [21–24]. Conventionally, they are prepared by the prolonged heating of aqueous solutions containing the ligand, $AuCl_4^-$, and excess PF_6^- (equation (1)). The resulting yellow solids are usually recrystallized to give analytically pure products.

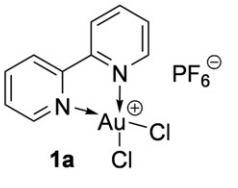


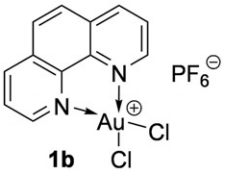
(1)

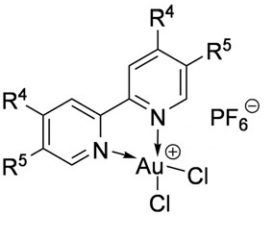
Microwave heating in closed vessels gave [AuCl$_2$(N–N)][PF$_6$] (**1a–1g**) in 93–99% yield (equation (2)). The reactions were complete within minutes and generally, the products were *analytically pure* yellow solids that did not require recrystallization. The only exception was **1e**, for which we found the conventional method to be superior (as all of our microwave-heated attempts gave **1e** that was impure). In the microwave-heated reactions, neutralization of the gold acid with $NaHCO_3$ (as in equation (1)) was not necessary or desirable. Neutralization prior to microwave heating gave **1a** that was contaminated with several percent of the hydrolyzed product [AuCl(OH)(2,2′-bipyridine)][PF$_6$], an impurity identified by its ^{1}H NMR spectrum [21].



(2)



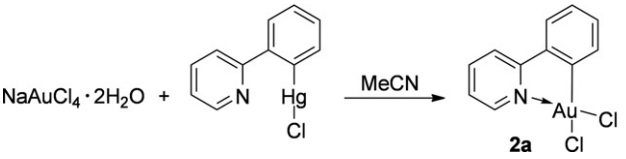




1c R^4 = Me R^5 = H
1d R^4 = OMe R^5 = H
1e R^4 = *t*-Bu R^5 = H
1f R^4 = H R^5 = Me
1g R^4 = Me R^5 = Me

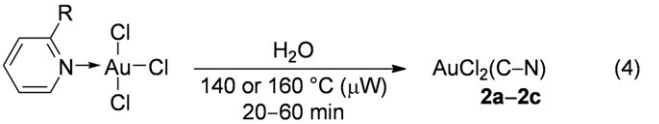
3.2. *$AuCl_2$(C–N)*

The neutral complex $AuCl_2$(ppy) (**2a**), containing a cyclometallated 2-phenylpyridine ligand, was first reported in 1989 [25]. This complex and its analogs are available in moderate to good yields (60–80%) *via* transmetallation from the corresponding ligand–mercury(II) chloride complexes (equation (3)) [29]. They may also be prepared directly from gold(III) and the ligands in refluxing aqueous solutions, *via* thermally activated cyclometallation, although the yields are often poor (20–40%) [26, 29]. A notable exception is $AuCl_2$(bnpy) (**2c**, containing cyclometallated 2-benzylpyridine), which was prepared in 80% yield from a refluxing aqueous solution of $AuCl_3 \cdot 2H_2O$ and the ligand [27]. An effective solvent-free synthesis of **2a** has been reported (involving conventional heating at 170°C), but the scope of the method has not been established [35]. Nevertheless, it is quite clear that *solvent-based* methods for the synthesis of $AuCl_2$(C–N) are lacking.

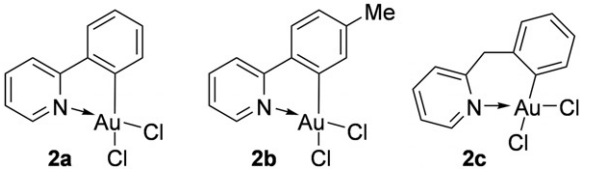


(3)

The $AuCl_3$ complexes of 2-phenylpyridine, 2-(*p*-tolyl)pyridine, 2-benzylpyridine, and 2-ethylpyridine, which have all been reported [25–28], precipitate *immediately* when the respective pyridines are added to aqueous $NaAuCl_4$ solutions (synthetic details may be found in Supplementary material, S2–S5). When aqueous suspensions of these complexes were heated to 140–160°C in sealed vessels in a microwave oven, the cyclometallated products **2a–2c** were obtained in 92–94% yield (*method A*, equation (4)). The pure products, light yellow or white solids, were obtained directly from the reaction mixtures with no need for recrystallization or further purification.

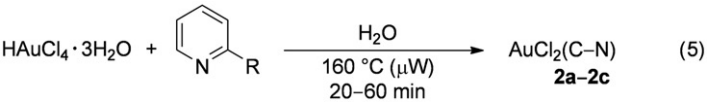


(4)



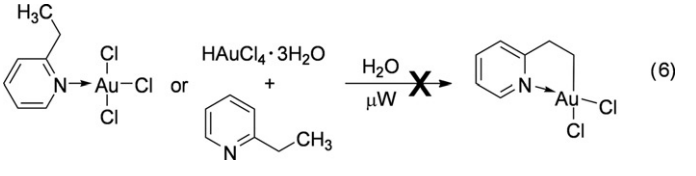
We have also found an *even more* convenient method for preparation of these complexes. When the appropriate ligands and the gold acid, $HAuCl_4 \cdot 3H_2O$, were subjected to the same reaction conditions, **2a–2c** were obtained in 78–87% yield

(*method B*, equation (5)). Presumably, the $AuCl_3$(ligand) complexes form as intermediates *in situ*.



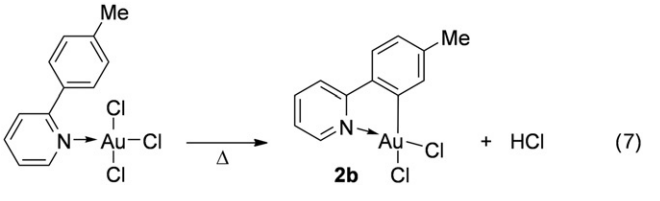
HCl, which is liberated during the course of these reactions, does not impede the formation of the cyclometallated products. Acceptable yields are obtained by both *methods A* and *B*, in which one and two equivalents of HCl are eliminated, respectively. A relevant factor is the inert nature of the resulting Au–C bonds. Constable reported, and we have again verified that, even in refluxing concentrated aqueous HCl, the Au–C bond in **2a** does not undergo protonolysis [25].

Encouraged by the above-described results, we attempted to perform cyclometallation with 2-ethylpyridine. However, all of our attempts, which started with either $AuCl_3$(2-ethylpyridine) or 2-ethylpyridine and the gold acid, were unsuccessful (equation (6)). Cinellu *et al.* [28] were also unable to achieve cyclometallation with $AuCl_3$(2-ethylpyridine). A successful cyclometallation would require activation of an sp^3 C–H bond in the methyl group of the ligand. The greater strength of these bonds compared to sp^2 C–H bonds provides an explanation for the failure of these attempts.



3.3. *Thermogravimetric analysis*

Intrigued by the high thermal stability of **2a–2c** (as suggested by the high temperatures of their syntheses), we studied one of these complexes, **2b**, by thermogravimetric analysis (TGA; Supplementary material, S6). It decomposed from 270°C to 320°C, liberating a mass corresponding to the ligand and one chlorine atom. When $AuCl_3$(2-(*p*-tolyl)pyridine) was examined (S7, figure 1), the cyclometallation reaction was observed. First, a mass corresponding to HCl was lost from 185°C to 235°C (equation (7)). The resulting **2b** then decomposed from 270°C to 320°C, as described above. In contrast, cyclometallation was not observed with $AuCl_3$(2-ethylpyridine) (S8). This complex decomposed before it could undergo cyclometallation, releasing a mass corresponding to the ligand and two chlorine atoms over the range 220–250°C.



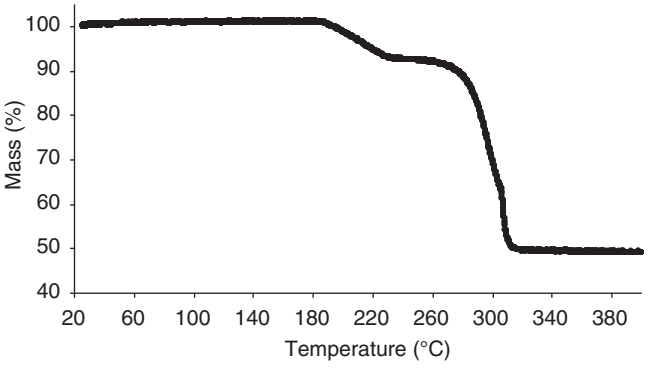


Figure 1. TGA of $AuCl_3$(2-(*p*-tolyl)pyridine).

The transformation of $AuCl_3$(2-phenylpyridine) to **2a** and its subsequent decomposition, as monitored by TGA, has been reported [24]. The authors noted the decomposition of **2a** to elemental gold above 360°C [24]. Curiously, we found that both **2b** and $AuCl_3$(2-ethylpyridine) gave a black residue upon decomposition which, according to the mass differences, was "AuCl" (S9).

4. Conclusion

We have developed new microwave methods for the synthesis of gold(III) complexes. The syntheses of both cationic and neutral gold(III) complexes were greatly improved by the use of microwave heating. We were pleased to find that these new methods can, in some cases, favorably replace procedures that employ toxic organomercury reagents. We hope that this report will encourage more researchers to experiment with microwave techniques for the synthesis of coordination complexes.

Supplementary material

Improved synthetic methods for 4,4′,5,5′-tetramethyl-2,2′-bipyridine, $AuCl_3$(2-phenylpyridine), $AuCl_3$(2-(*p*-tolyl)pyridine), $AuCl_3$(2-benzylpyridine), and $AuCl_3$(2-ethylpyridine). Thermogravimetric analyses of **2b**, $AuCl_3$(2-(*p*-tolyl)pyridine), and $AuCl_3$(2-ethylpyridine). ^{1}H and COSY NMR spectra of $AuCl_3$(2-(*p*-tolyl)pyridine), **2b**, $AuCl_3$(2-benzylpyridine), and **2c**. These materials, S1–S17, are available in the online version of this article.

Acknowledgments

We thank the *GASSMAKS* program of the Norwegian Research Council (grant no. 185513/I30) for generous financial support. We thank Osamu Sekiguchi for mass

spectrometry and Sharmala Aravinthan for thermogravimetric analysis. We thank Ajay Venugopal, Manik Kumer Ghosh, and Ole Swang for useful discussions.

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