Synthesis and Solution Behavior of some Bis[2-{(dimethylamino)methyl}phenyl]gold(III) Complexes

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Abstract

$[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ reacts with $[Hg(2\text{-}C_6H_4CH_2NMe_2)_2]$ (2/1) or with $[Hg(2\text{-}C_6H_4CH_2NMe_2)Cl]$ (1/1) both in the presence of an excess of $[Me_4N]Cl$ to give $[Au(2\text{-}C_6H_4CH_2NMe_2)_2Cl]$ (1) which reacts with KCN or $AgClO_4$ to give $[Au(2\text{-}C_6H_4CH_2NMe_2)_2CN]$ (2) or $[Au(2\text{-}C_6H_4CH_2NMe_2)_2]ClO_4$ (3), respectively. The solution behavior of these complexes is studied by NMR spectroscopy.

Introduction

We have reported the use of arylmercury compounds to prepare mono- and di- (homo and hetero) aryl complexes [1, 2]. In particular, we have prepared arylgold(I) and gold(III) complexes [1]. Those of gold(III) are obtained by the following reactions

$$[AuCl_4]^- + 2R_2Hg \longrightarrow [AuR_2Cl_2]^- + 2RHgCl \quad (1)$$

R = $2\text{-}C_6H_4NO_2$; $C_6H_4NO_2\text{-}2$, Me-6 [1a]

$$[AuCl_4]^- + R_2Hg \xrightarrow{-Cl^-} [AuRCl_2] + RHgCl \quad (2)$$

R = $2\text{-}C_6H_4N{=}NPh$ [1b]; $2\text{-}C_6H_4CH_2NMe$ [1c]

$$[AuRCl_2] + R'_2Hg \longrightarrow [Au(R)(R')Cl] \quad (3)$$

R = $2\text{-}C_6H_4CH_2NMe_2$; R' = $2\text{-}C_6H_4N{=}NPh$ [1d], Ph [1e], C_6F_5 [1f] $2\text{-}C_6H_4NO_2$ [1g]; R = R' = $2\text{-}C_6H_4N{=}NPh$ [1h]

In this paper we report the study of the reaction of type (3) when R = R' = $2\text{-}C_6H_4CH_2NMe_2$. Because the N → Au bond is unaffected in all the reactions we made with the starting complex $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ and also with all of its derivatives $[Au(2\text{-}C_6H_4CH_2NMe_2)(R)Cl]$ we thought that the synthesis of $[Au(2\text{-}C_6H_4CH_2NMe_2)_2Cl]$ (1) would be of interest to prepare pentacoordinated gold(III) complexes.

In addition, we planned this reaction to determine the limits of the 'organomercury route' for the synthesis of arylgold(III) complexes. We had some previous data about the difficulty of transmetallating the $2\text{-}C_6H_4CH_2NMe_2$ group to an arylgold(III) complex. Thus for example, (i) by reacting equimolecular amounts of $[Hg(2\text{-}C_6H_4N{=}NPh)_2]$ with $[AuCl_4]^-$ at room temperature we had obtained $[Au(2\text{-}C_6H_4N{=}NPh)_2Cl]$ [1h] while under the same conditions $[Hg(2\text{-}C_6H_4CH_2NMe_2)_2]$ gave only the monoaryl complex $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ [1c], (ii) the reaction of the same mercurial with $[Au(C_6F_5)Cl_3]^-$ led to metallic gold at room temperature [1f], and (iii) by reacting $[Hg(2\text{-}C_6H_4CH_2NMe_2)_2]$ and $[Au(2\text{-}C_6H_4N{=}NPh)Cl_2]$ the complex $[Au(2\text{-}C_6H_4CH_2NMe_2)(2\text{-}C_6H_4N{=}NPh)Cl]$ is obtained in low yield because metallic gold is also formed. However, the same complex can be obtained in high yield by reacting $[Hg(2\text{-}C_6H_4N{=}NPh)_2]$ and $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ [1d].

Experimental

Recording of the IR spectra, the C, H and N analyses, conductance measurements, and the melting point determinations were performed as described elsewhere [1]. NMR spectra were recorded in a Brucker AC-200 FT spectrometer. Reactions were carried out with magnetic stirring without special precautions to exclude air. The three complexes are white solids. Protons of $2\text{-}C_6H_4CH_2NMe_2$ groups on complexes 1 and 2 are named according to Figs. 1 and 2, respectively.

$[Au(2\text{-}C_6H_4CH_2NMe_2)_2Cl]$ (1)

To a solution of $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ [1c] (100 mg, 0.25 mmol) in acetone (20 cm^3) solid $[Hg(2\text{-}C_6H_4CH_2NMe_2)_2]$ [3] (59 mg, 0.13 mmol)

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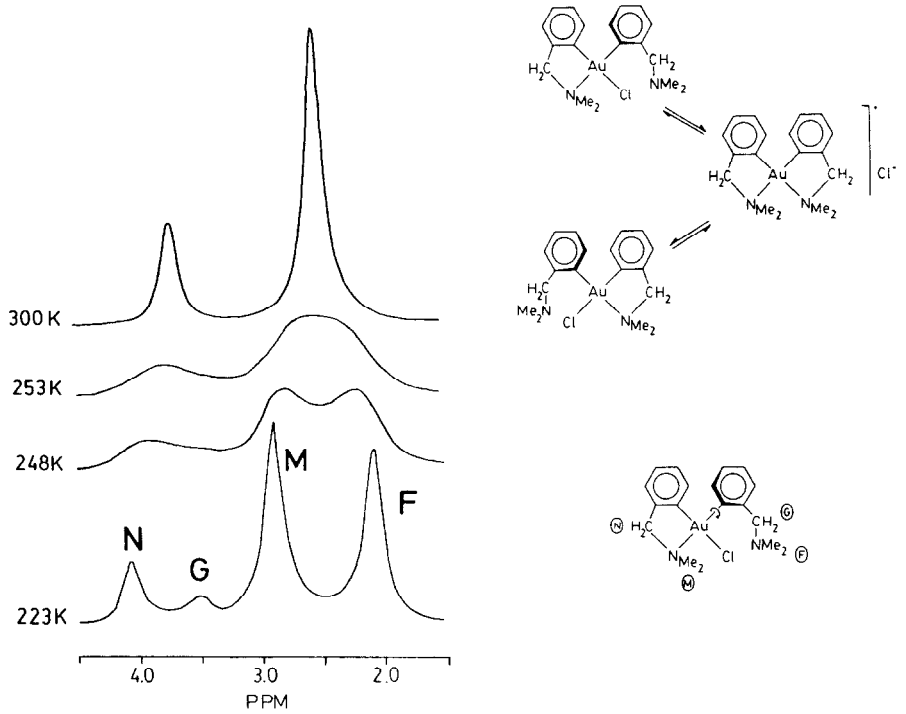

Fig. 1. Proposed fluxional behavior of complex **1**.

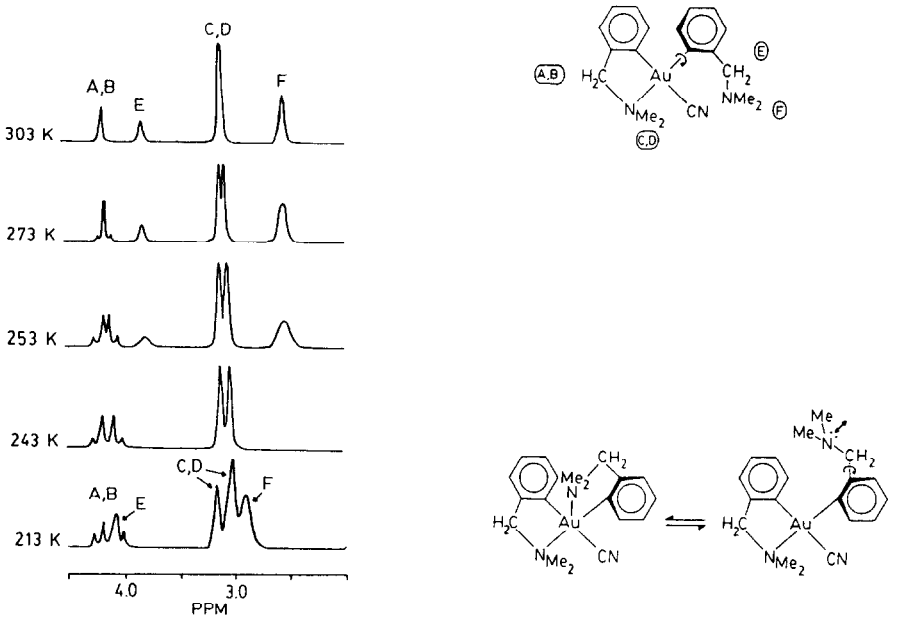

Fig. 2. Proposed fluxional behavior of complex **2**.

and $[Me_4N]Cl$ (69 mg, 0.25 mmol) were added. After 3.5 h of refluxing the solvent was evaporated and the residue extracted with dichloromethane (3 X 5 cm^3), filtered off and the resulting solution concentrated (1 cm^3). Addition of n-hexane (15 cm^3) gives complex **1** in 55% yield. *Anal.* Found: C, 42.53; H, 4.76; N, 5.42; Au, 39.12. Calc. for $C_{18}H_{24}AuClN_2$: C, 43.17; H, 4.83; N, 5.59; Au, 39.33%. NMR (CD_2Cl_2, ppm) ^1H, 300 K: δ 2.54 (s, 12H, Me), 3.73 (s, 4H, CH_2), 6.9–7.1 (m, 8H, C_6H_4). 223 K: δ 2.05 (s, 6H, G Me), 2.90 (s, 6H, M Me), 3.49 (s, 2H, F CH_2), 4.07 (s, 2H, N CH_2). ^{13}C, 300 K: δ 47.7 (Me), 69.2 (CH_2), 126.4, 127.7, 133.2, 144.0 (C3–C6) 126.5, 142.7 (C1, C2). 223 K: δ 45.0, 49.4 (Me), 66.0, 70.4 (CH_2).

[Au(2-$C_6H_4CH_2NMe_2$)$_2$CN] (2)

To a solution of complex **1** (40 mg, 0.08 mmol) in acetone (10 cm^3) solid KCN (13 mg, 0.2 mmol) was added. After 72 h the resulting suspension was concentrated to dryness and the residue extracted with dichloromethane (3 × 5 cm^3) and filtered off. The resulting solution was concentrated (1 cm^3) and n-hexane added to precipitate complex **2** in 63% yield. *Anal.* Found: C, 46.28; H, 4.98; N, 9.20. Calc. for $C_{19}H_{24}AuN_3$: C, 46.44; H, 4.92; N, 8.55%. NMR (CD_2Cl_2, ppm) ^{1}H, 303 K: δ 2.56 (s, 6H, F Me), 3.15 (s, 6H, CD Me), 3.75 (s, 2H, E CH_2), 4.16 (s, 2H, AB CH_2) 6.5–7.1 (m, 8H, C_6H_4). 273 K: δ 2.54 (br, s, 6H, F Me), 3.11, 3.15 (s, 6H, C and D Me), 3.74 (br, s, 2H, E CH_2), 4.07, 4.146, 4.152, 4.22 (AB system, 2H, A and B CH_2, J_{AB} = 14 Hz). 213 K: δ 2.91 (s, 6H, F Me), 3.02, 3.18 (s, 6H, C and D Me), 4.01, 4.08, 4.18, 4.25 (AB system, 2H, A and B CH_2, J_{AB} = 14 Hz), 4.08 (s, 2H, E CH_2).

[Au(2-$C_6H_4CH_2NMe_2$)$_2$]ClO_4 (3)

To a solution of complex **1** (91 mg, 0.18 mmol) in acetone (10 cm^3) solid $AgClO_4$ (37 mg, 0.18 mmol) was added. After 30 min in the dark the resulting suspension was concentrated to dryness and the residue extracted with dichloromethane (3 × 5 cm^3) and filtered off. The resulting solution was concentrated (1 cm^3) and diethyl ether added to precipitate complex **3** in 22% yield, melting point 124 °C dec. *Anal.* Found: C, 38.63; H, 4.29; N, 5.16. Calc. for $C_{18}H_{24}AuClN_2O_4$: C, 38.48; H, 4.31; N, 4.99%. NMR (CD_2Cl_2, ppm) ^{1}H, 300 K: δ 3.15 (s, 12H, Me), 4.20 (s, 4H, CH_2), 6.7–7.4 (m, 8H, C_6H_4).

Results and Discussion

As mentioned above [Hg(2-$C_6H_4CH_2NMe_2$)$_2$] reacts with $[AuCl_4]^-$ (1:1, dichloromethane, 24 h, room temperature) to give [Au(2-$C_6H_4CH_2NMe_2$)Cl_2] [1c]. The expected complex, [Au(2-$C_6H_4CH_2NMe_2$)$_2$Cl] (**1**), could not be prepared by reacting [Hg(2-$C_6H_4CH_2NMe_2$)$_2$] with [Au(2-$C_6H_4CH_2NMe_2$)Cl_2] (1:1, acetone, 24 h, room temperature). However, this last reaction gives complex **1** if the temperature is raised to that of refluxing of the solvent.

$$[Hg(2\text{-}C_6H_4CH_2NMe_2)_2] + [Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2] \longrightarrow \underset{\mathbf{1}}{[Au(2\text{-}C_6H_4CH_2NMe_2)_2Cl]} + [Hg(2\text{-}C_6H_4CH_2NMe_2)Cl]$$

Because [Hg(2-$C_6H_4CH_2NMe_2$)Cl] symmetrizes in the presence of Cl^- the synthesis of complex **1** can be achieved

$$2[Hg(2\text{-}C_6H_4CH_2NMe_2)Cl] + Cl^- \longrightarrow [Hg(2\text{-}C_6H_4CH_2NMe_2)_2] + [HgCl_3]^-$$

through two other routes: (i) by using a 1:2 molar ratio of the reagents in the presence of excess of $[Me_4N]Cl$

$$[Hg(2\text{-}C_6H_4CH_2NMe_2)_2] + 2[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2] \xrightarrow{+Cl^-} 2[Au(2\text{-}C_6H_4CH_2NMe_2)_2Cl] + [HgCl_3]^-$$

or (ii) by using [Hg(2-$C_6H_4CH_2NMe_2$)Cl] as transmetallating agent in the presence of excess of $[Me_4N]Cl$:

$$[Hg(2\text{-}C_6H_4CH_2NMe_2)Cl] + [Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2] \xrightarrow{+Cl^-} [Au(2\text{-}C_6H_4CH_2NMe_2)_2Cl] + [HgCl_3]^-$$

Unlike other similar arylgold(III) complexes, complex **1** is soluble in diethyl ether and slightly soluble in n-hexane.

Complex **1** reacts with excess of KCN or $AgClO_4$ (1:1) to give [Au(2-$C_6H_4CH_2NMe_2$)$_2$CN] (**2**) or [Au(2-$C_6H_4CH_2NMe_2$)$_2$]ClO_4 (**3**), respectively.

The infrared spectrum of complex **1** shows a band at 300(vs) cm^{-1} which coincides with the one in the complex [Au(2-$C_6H_4CH_2NMe_2$)Cl_2] which is assigned to the ν(AuCl) mode *trans* to the phenyl group [1c] and also with that found in [Au(2-$C_6H_4CH_2NMe_2$)(Ph)Cl] which crystal structure [1e] shows the chloro ligand *trans* to the phenyl group of the 2-$C_6H_4CH_2NMe_2$ ligand. Because the ν(AuCl) frequency is quite sensitive to the coordination number of the gold atom [1d] the above mentioned coincidence would require that one of the 2-$C_6H_4CH_2NMe_2$ ligands be monocoordinated. This is also the structure in solution at low temperature (see below). The band at 350(s) cm^{-1} in [Au(2-$C_6H_4CH_2NMe_2$)Cl_2], assigned to the ν(AuCl) mode *trans* to the nitrogen atom [1c], is not observed in complex **1**.

Complexes **2** and **3** lack the 300 cm^{-1} band of complex **1**, and show those characteristic of CN (2130(w) cm^{-1}) and ClO_4 (1080(br,vs) and 620(s) cm^{-1}), respectively.

In acetone solutions, complexes **1** and **2** are nonconducting while **3** is a 1:1 electrolyte (Λ_M = 103 Ω^{-1} cm^2 mol^{-1}) according to the proposed formulations.

The NMR spectra in CD_2Cl_2 of complexes **1** and **2** are temperature dependent, whilst that of complex **3** is not. As expected ^1H and ^{13}C NMR spectra of complex **1** show two singlets corresponding to methyl and methylene protons or carbon atoms, respectively. At low temperature (223 K), the ^1H NMR spectrum of complex **1** shows four singlets corresponding to two different Me and CH_2 groups (see Fig. 1). This can be interpreted as the result of being one of the $2\text{-}C_6H_4CH_2NMe_2$ ligands chelating and the other monocoordinated. This one should be rotating around the C–Au bond. The spectrum changes when the temperature is raised to give, at 300 K, two singlets with the coalescence temperature at 250 K. The spectrum at 300 K is the result of a rapid dynamic equilibrium in which both $2\text{-}C_6H_4CH_2NMe_2$ ligands become equivalent as in the cation of complex **3**. An intermediate such as $[Au(2\text{-}C_6H_4CH_2NMe_2)_2]Cl$ could be postulated as the responsible of the process, although its presence in the equilibrium should be in trace amounts because complex **1** is non-conducting in acetone solution.

The ^1H NMR spectrum of complex **2** shows, at 303 K, four singlets corresponding, respectively, to the Me and CH_2 groups of two different $2\text{-}C_6H_4CH_2NMe_2$ groups, such as the low temperature structure of complex **1** (see Fig. 2). The lowering of the temperature causes the following changes: the low field methylene and methyl resonances change to an AB system and two singlets, respectively, due to a chelating $2\text{-}C_6H_4CH_2NMe_2$ group while the high field ones, due to the monocoordinated $2\text{-}C_6H_4CH_2NMe_2$ group, widen, disappear (coalescence temperature 243 K) and, finally at 213 K, appear as singlets at higher field (near to the resonances due to the coordinated group) which can be interpreted as the result of the change of the C–Au rotation of the $2\text{-}C_6H_4CH_2NMe_2$ group to a movement consisting of: N–Au coordination → cleavage of the N–Au bond → inversion at the nitrogen atom → rotation around the C–N bond → N–Au coordination. The differences between complexes **1** and **2** are certainly due to the stronger nature of the Au–CN compared to the Au–Cl bonds.

The dynamic behavior reported here is similar to that observed in tin(IV) complexes containing ligands related to $2\text{-}C_6H_4CH_2NMe_2$ [4].

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