2-[(DIMETHYLAMINO)METHYL]PHENYLGOLD(III) COMPLEXES

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Summary

[Hg(2-C$_6$H$_4$CH$_2$NMe$_2$)Cl] reacts with Me$_4$N[AuCl$_4$] or with [AuCl$_3$(tht)] (tht = tetrahydrothiophene) in the presence of Me$_4$NCl to give [Au(2-C$_6$H$_4$CH$_2$NMe$_2$)Cl$_2$]. The same complex can also be obtained by treating [Hg(2-C$_6$H$_4$CH$_2$NMe$_2$)$_2$] with Me$_4$N[AuCl$_4$]. The reactions of [Au(2-C$_6$H$_4$CH$_2$NMe$_2$)Cl$_2$] with (i) KBr, KI or AgOOCCH$_3$ give [Au(2-C$_6$H$_4$CH$_2$NMe$_2$)X$_2$] (X = Br, I, OOCCH$_3$), (ii) with PPh$_3$ give [Au(2-C$_6$H$_4$CH$_2$NMe$_2$)Cl(PPh$_3$)]Cl and (iii) with AsPh$_3$, py or tht in the presence of NaClO$_4$ lead to the cationic complexes [Au(2-C$_6$H$_4$CH$_2$NMe$_2$)Cl(L)]ClO$_4$.

Introduction

2-[(Dimethylamino)methyl]phenyl complexes have been obtained by *ortho-* or *trans*-metallation reactions using the corresponding lithium derivatives [1]. In spite of the high reactivity of anhydrous gold(III) halides towards benzene to give phenylgold(III) complexes [2] these auration reactions are inhibited by the presence of a coordinating substituent in the aromatic ring [3,4]. In fact *N, N*-dimethylbenzylamine reacts with gold(III) bromide or chloride to give trihalogold(III) complexes containing the amine as a ligand or the ammonium [AuX$_4$]$^-$ or [AuX$_2$]$^-$ salts [4], but *ortho*-metallated complexes (i.e. 2-[(dimethylamino)methyl] complexes) were not obtained. Similar results were obtained when azobenzene was used [4–6]. We have recently shown that the *ortho*-metallated complex dichloro[2-(phenylazo)phenyl]gold(III) can be obtained by using chloro[2-phenylazo)phenyl]mercury [7]. In the present paper we present a new method for preparing complexes of 2-[(dimethylamino)methyl]phenyl using its mercury derivatives as arylating agents, and the synthesis of the first such derivatives of gold(III).
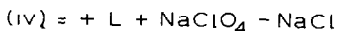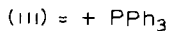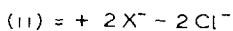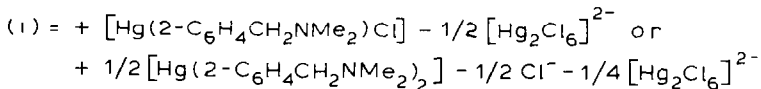
Results and discussion

When [AuCl$_3$(tht)] (tht = tetrahydrothiophene), [Hg(2-C$_6$H$_4$CH$_2$NMe$_2$)Cl] [8] and Me$_4$Cl are reacted in acetone (1/1/1) Me$_4$N[Hg$_2$Cl$_6$] precipitates and a

solution of the complex [Au(2-C$_6$H$_4$CH$_2$NMe$_2$)Cl$_2$] (I) is obtained. The complex can also be prepared by reacting Me$_4$N[AuCl$_4$] with [Hg(2-C$_6$H$_4$CH$_2$NMe$_2$)Cl] (1/1), or with [Hg(2-C$_6$H$_4$CH$_2$NMe$_2$)$_2$] [9] (1/1 or 2/1).

When [AuCl$_3$(tht)] or Me$_4$N[AuCl$_4$] were treated in diethyl ether with Li(2-C$_6$H$_4$CH$_2$NMe$_2$) [9] (1/1), immediate precipitation of gold or unidentified species which contain lithium were obtained. Complex I was not detected.

The reactions of I with KBr (1/3.5), KI (1/2) or AgOOCCH$_3$ (1/2) in acetone give complexes [Au(2-C$_6$H$_4$CH$_2$NMe$_2$)X$_2$] [X = Br (II), I (III), CH$_3$COO (IV)] (see

SCHEME 1

L = PPh$_3$ (VI), AsPh$_3$ (VII),
py (VIII), tht (IX)

(i) = + [Hg(2-C$_6$H$_4$CH$_2$NMe$_2$)Cl] − 1/2 [Hg$_2$Cl$_6$]$^{2-}$ or

+ 1/2 [Hg(2-C$_6$H$_4$CH$_2$NMe$_2$)$_2$] − 1/2 Cl$^-$ − 1/4 [Hg$_2$Cl$_6$]$^{2-}$

(ii) = + 2 X$^-$ − 2 Cl$^-$

(iii) = + PPh$_3$

(iv) = + L + NaClO$_4$ − NaCl
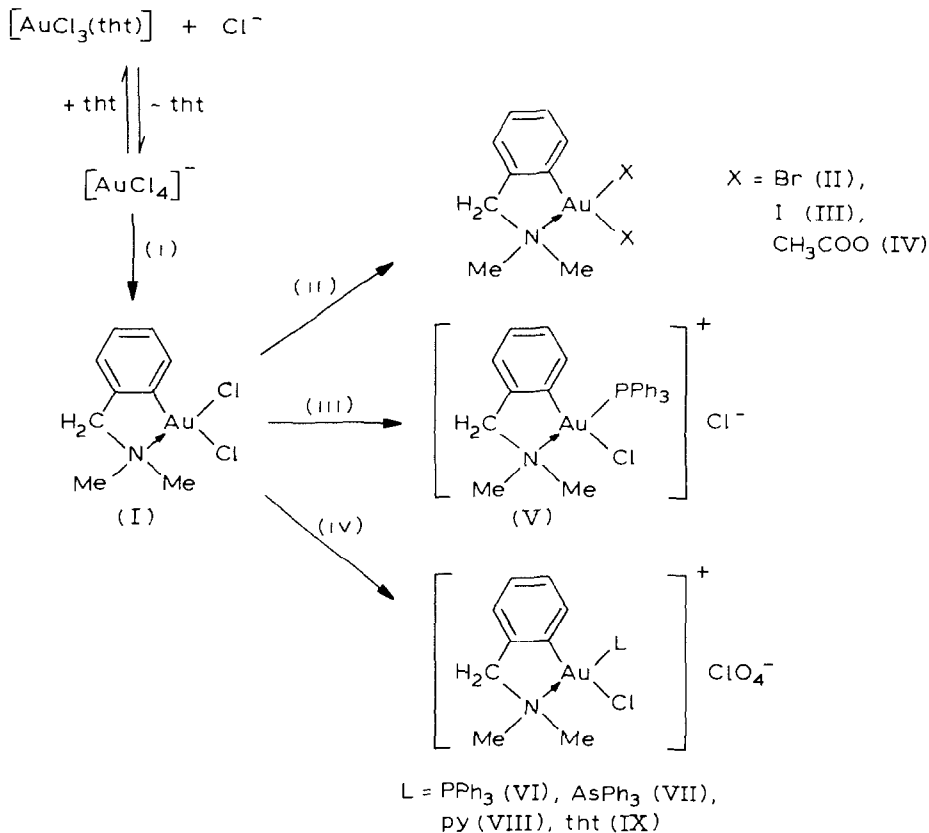
Scheme 1). Complexes I–IV are non-conducting in acetone solution. The ^{1}H NMR spectrum of I in acetone-d_6 (TMS) shows peaks at δ 3.26 (s, 6H, CH$_3$), 4.63 (s, 2H, CH$_2$), 6.54 (m, 3H, 3-, 4- and 5-phenyl protons) and 7.18 (d, 1H, 6-phenyl proton)

ppm, assigned according to the spectra of related complexes [10]. The ^{1}H NMR spectrum of II is identical to that of I. The complex III is unstable in solution. The main difference between the IR spectra of I and II, III or IV is the presence of two strong bands at 350 and 300 cm^{-1} in I; these can be assigned to ν(AuCl) *trans* to N and phenyl, respectively. Such a great difference in the position of the bands is in accordance with the stronger *trans*-influence of phenyl with respect to N-donor ligands. In the related [Au(2-C_6H_4N=NC_6H_5)Cl$_2$] complex they appear, respectively, at 370 and 305 cm^{-1} [7]. The corresponding ν(Au–Br) and ν(Au–I) in II and III are expected to fall below the range of our spectrophotometer. Complex IV shows strong bands at 1670, 1620 [ν_{asym}(CO$_2$)] 1370 and 1315 [ν_{sym} (CO$_2$)] cm^{-1}.

The reaction between I and PPh$_3$ (1:1) in dichloromethane gives the cationic complex [Au(2-C_6H_4CH$_2$NMe$_2$)Cl(PPh$_3$)]Cl (V) that shows a strong band at 310 cm^{-1} in its IR spectrum. According to the assignment made for I this band corresponds to ν(AuCl) *trans* to the phenyl group. The reaction of [Pd(2-C_6H_4CH$_2$NMe$_2$)Cl]$_2$ with PPh$_3$ leads to [Pd(2-C_6H_4CH$_2$NMe$_2$)Cl(PPh$_3$)], where the chloro-ligand is also *trans* to the phenyl group [11].

[Au(2-C_6H_4CH$_2$NMe$_2$)Cl(PPh$_3$)]ClO$_4$ (VI) can be obtained by reacting V with NaClO$_4$ (1/1) in acetone or I with PPh$_3$ and NaClO$_4$ (1/1/1) in acetone.

Complex I reacts neither with poorer donor ligands (such as AsPh$_3$, py or tht) nor with NaClO$_4$, but it does react with the neutral ligands in the presence of NaClO$_4$ (1/1/1), leading to complexes of the type [Au(2-C_6H_4CH$_2$NMe$_2$)Cl(L)]ClO$_4$ [L = AsPh$_3$ (VII), py (VIII), tht (IX)]. Complexes VIII and IX show a band at 315 and 307 cm^{-1}, respectively, that can also be assigned to ν(AuCl) *trans* to the phenyl group. The corresponding ν(AuCl) in VII is masked by several bands corresponding to AsPh$_3$. Scheme 1 summarizes the reactions leading to complexes I–IX.

The reactivity of I is quite different from that of the related [Au(2-C_6H_4N=N–C_6H_5)Cl$_2$] [7], because this complex reacts (i) with PPh$_3$ or AsPh$_3$ (1/1) to give complexes of the [Au(2-C_6H_4N=N–C_6H_5)Cl$_2$L] type by cleavage of the Au–N bond, and (ii) with PPh$_3$ (1/2) to give the cationic complex *trans*-[Au(2-C_6H_4N=NC_6H_5)Cl(PPh$_3$)$_2$]$^+$ only in the presence of NaClO$_4$ otherwise the neutral adduct [Au(2-C_6H_4N=N–C_6H_5)Cl$_2$(PPh$_3$)] is isolated. With I the cleavage of the Au–N bond is not observed, even if a molar ratio PPh$_3$/I of 2/1 is used, and only V is isolated. Similar results have been observed for the corresponding palladium complexes [11,12].

Experimental

IR spectra were recorded on a Perkin–Elmer 457 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in 5×10^{-4} M solutions with a Philips 9501 conductimeter. Melting points were determined on a Reichert apparatus and are uncorrected. C, H and N analyses were carried out with a Perkin–Elmer 240C microanalyzer. Au was determined by ashing the samples with an aqueous solution of hydrazine. Solvents were distilled before use. All the reactions were carried out at room temperature. The recipes are for the highest yield method. The analytical data are reported as found (calcd.) $\pm 0.05\%$.

[Au(2-C_6H_4CH$_2$NMe$_2$)Cl$_2$] (I). To a solution of [AuCl$_3$(tht)] (202 mg, 0.52 mmol) in acetone (15 ml), the solids [Hg(2-C_6H_4CH$_2$NMe$_2$)Cl] (194 mg, 0.52 mmol)

and Me$_4$NCl (57 mg, 0.52 mmol) were added, the resulting suspension was stirred for 24 h and then concentrated to dryness. The residue was extracted with dichloromethane (5 × 5 ml) and the extract was concentrated (5 ml). Addition of diethyl ether (15 ml) caused precipitation of a white crystalline solid, which was filtered off and washed with diethyl ether to give I (88% yield), m.p. 185°C (d). Anal.: C, 27.45 (26.90); H, 3.25 (3.00); N, 3.55 (3.50); Au, 48.25 (49.00%).

[Au(2-C$_6$H$_4$CH$_2$NMe$_2$)Br$_2$] (II). To a solution of I (50 mg, 0.12 mmol) in acetone (12 ml) solid KBr (52 mg, 0.43 mmol) was added, the resulting suspension stirred for 6 h and then concentrated to dryness. The residue was extracted with dichloromethane (3 × 5 ml) and the extract was concentrated (1 ml). Addition of diethyl ether (10 ml) caused precipitation of a yellow solid, which was filtered off, washed with diethyl ether and recrystallized from dichloromethane/diethyl ether to give II (93% yield), m.p. 172°C (d). Anal.: C, 22.55 (22.05); H, 2.95 (2.45); N, 2.75 (2.85); Au, 39.80 (40.10%).

[Au(2-C$_6$H$_4$CH$_2$NMe$_2$)I$_2$] (III). To a solution of I (60 mg, 0.15 mmol) in acetone (10 ml) solid KI (50 mg, 0.30 mmol) was added, the resulting suspension stirred for 15 min and filtered. The filtrate was concentrated (1 ml) and addition of diethyl ether (10 ml) caused precipitation of III as a red solid (80% yield), m.p. 105°C (d). Anal.: C, 19.10 (18.50); H, 2.40 (2.05); N, 2.20 (2.40); Au, 34.00 (33.65%).

[Au(2-C$_6$H$_4$CH$_2$NMe$_2$)(OOCH$_3$)$_2$] (IV). To a solution of I (56 mg, 0.14 mmol) in acetone (10 ml), solid AgOOCCH$_3$ (58 mg, 0.34 mmol) was added, the resulting suspension stirred for 3 h under N$_2$ and then concentrated to dryness. The residue was treated as described for II, to give IV as a white solid (67% yield), m.p. 135°C (d). Anal.: C, 35.35 (34.75); H, 4.35 (4.05); N, 3.15 (3.10); Au, 43.55 (43.85%).

[Au(2-C$_6$H$_4$CH$_2$NMe$_2$)Cl(PPh$_3$)]Cl (V). To a suspension of I (40 mg, 0.10 mmol) in dichloromethane (20 ml) solid PPh$_3$ (26 mg, 0.10 mmol) was added, the resulting solution stirred for 30 min and then concentrated to 1 ml. Addition of diethyl ether (10 ml) caused precipitation of a solid, which was filtered off and washed with diethyl ether to give V as a yellow solid (91% yield), m.p. 174°C, which was recrystallized from dichloromethane/diethyl ether. $\Lambda_M = 165$ Ω^{-1} cm^2 mol^{-1} (4 × 10^{-4} M in acetonitrile). Anal.: C, 48.50 (48.80); H, 4.55 (4.10); N, 1.50 (2.10); Au, 29.15 (29.65%).

[Au(2-C$_6$H$_4$CH$_2$NMe$_2$)Cl(PPh$_3$)]ClO$_4$ (VI). To a solution of I (50 mg, 0.12 mmol) in acetone (7 ml), the solids PPh$_3$ (33 mg, 0.12 mmol) and NaClO$_4$ (15 mg, 0.12 mmol) were added, the resulting suspension stirred for 30 min and then concentrated to dryness. The residue was treated as described for II to give VI as a white solid (86% yield), m.p. 140°C(d). $\Lambda_M = 104$ Ω^{-1} cm^2 mol^{-1} (3.5 × 10^{-4} M in acetone). Anal.: C, 45.25 (44.50); H, 4.35 (3.75); N, 1.80 (1.90); Au, 26.70 (27.05)%.

[Au(2-C$_6$H$_4$CH$_2$NMe$_2$)Cl(L)]ClO$_4$ (VII-IX). To solutions of I (0.1 mmol) in acetone (10 ml) were added a stoichiometric amount (AsPh$_3$) or an excess (py, tht) of the ligand and stoichiometric amounts of NaClO$_4$, and the resulting suspension was stirred (14 h for VII and IX or 1 h for VIII) and then filtered. The residues were treated as described for II to give VII–IX as white solids (78, 70 and 54% yield), m.p. 187°C(d), 175°C(d) and 178°C(d), respectively. $\Lambda_M = 107$, 115 and 109 Ω^{-1} cm^2 mol^{-1} (3–4 × 10^{-4} M in acetone), respectively. Anal.: VII C, 42.45 (41.95); H, 3.90 (3.50); N, 1.75 (1.80); Au, 25.20 (25.50%); VIII C, 31.35 (30.85); H, 3.00 (3.15); N, 4.50 (5.15); Au, 35.75 (36.15%); IX C, 28.45 (28.15); H, 3.65 (3.65); H, 2.75 (2.55); Au, 35.05 (35.55%).

Acknowledgement

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