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Synthesis of [2-{(dimethylamino)methyl}phenyl]-(2-nitrophenyl)gold(III) complexes

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Abstract

$[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ reacts with $[Hg(2\text{-}C_6H_4NO_2)_2]$ and $(Me_4N)Cl$ (2/1/2) to give $[Au(2\text{-}C_6H_4CH_2NMe_2)(2\text{-}C_6H_4NO_2)Cl]$ (I). Metathetical reactions of I with AgAc ($Ac = OOCCH_3$), KBr or KI give complexes $[Au(2\text{-}C_6H_4CH_2NMe_2)(2\text{-}C_6H_4NO_2)X]$ (X = Ac (II), Br (III), I (IV)), all of which are obtained as mixtures of two isomers. The reaction of I with PPh_3 (1/1) gives $[Au(2\text{-}C_6H_4CH_2NMe_2)(2\text{-}C_6H_4NO_2)Cl(PPh_3)]$ (V), which reacts with $NaClO_4$ (1/1) to give $[Au(2\text{-}C_6H_4CH_2NMe_2)(2\text{-}C_6H_4NO_2)(PPh_3)]ClO_4$ (VI). This can also be obtained directly by treating I with PPh_3 and $NaClO_4$ (1/1/1). A similar method ($I + L + AgClO_4$) can be used to prepare $[Au(2\text{-}C_6H_4CH_2NMe_2)(2\text{-}C_6H_4NO_2)(py)]ClO_4$ (py = pyridine) (VII).

Introduction

We have demonstrated the value of arylmercury compounds as transmetallating reagents for the synthesis of aryl-gold(I) and -gold(III) [1] complexes. One of their applications is in the synthesis of mixed diarylgold(III) complexes by introduction of the aryl groups in the two-step process (1)

$$\begin{tikzcd}
{[AuCl_4]^- + R_2Hg} \arrow[r, "-RHgCl", "-Cl^-"'] & {[Au(R)Cl_2]} \arrow[r, "+R'_2Hg", "-R'HgCl"'] & {[Au(R)(R')Cl]} \arrow[d, "(2)"', "+L"] \\
 & & {R—R' + [AuCl(L)]}
\end{tikzcd} \tag{1}$$

The interest in such compounds arises from their use as precursors for the synthesis of biphenyl derivatives R–R′ [2]. Our method involving reaction 2 is, probably the mildest of all those reported [3]. However, to establish synthetic scope

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of these mixed diarylgold(III) complexes and their derivatives it is necessary to investigate, first, the ability of the organomercury compounds to provide access to such compounds and, second, the best conditions for preparing the gold complexes to be used as starting material.

The two step method for the synthesis of mixed diarylgold(III) complexes is unsuitable when R = 2-$C_6H_4NO_2$ because, even if the molar ratio between $[AuCl_4]^-$ and R_2Hg is 1/1 the diaryl complex $[Au(2\text{-}C_6H_4NO_2)_2Cl_2]^-$ is obtained [4]. We have observed a similar double arylation in reactions between $[Hg(2\text{-}C_6H_4NO_2)_2]$ and $PdCl_2$ [5], or $PtCl_2$ [6], or $RhCl_3$ [7]. Thus, the method is restricted to those R_2Hg compounds that lead, in the first step, to a monoarylgold(III) complex. We have found that this is the case for R = 2-$C_6H_4N{=}NPh$ [8] and 2-$C_6H_4CH_2NMe_2$ [9]. Starting from $[Au(2\text{-}C_6H_4N{=}NPh)Cl_2]$ we prepared the diaryl derivatives with R′ = 2-$C_6H_4N{=}NPh$ [10] and 2-$C_6H_4CH_2NMe_2$ [11], but in trying to prepare those with R′ = Ph undergo decomposition [2], while with R′ = 2-$C_6H_4NO_2$ or C_6F_5 in acetone activation of a C–H bond of acetone occurs, leading to $[Au(2\text{-}C_6H_4N{=}NPh)(CH_2C(O)CH_3)Cl]$ [1]. When $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ was used the mixed diaryl complexes with R′ = Ph [2] or C_6F_5 [12] were obtained even in acetone.

In this paper we describe the reactions carried out for compounds when R′ = 2-$C_6H_4NO_2$. These reactions were designed to meet several objectives, in addition of those mentioned above. Firstly, we aimed to complete the sequence of reactions which would allow comparison of the behaviour of $[Au(2\text{-}C_6H_4N{=}NPh)Cl_2]$ and $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ in respect of the C–H activation in the acetone. Secondly we aimed to prove that the second transmetallation would occur, which, could not be regarded as certain in view of the difficulty of transferring this group from mercury to other metal centres (e.g. Au^{III} [4] or Sn^{IV} [13]). Finally, we hoped to see whether once the 2-$C_6H_4NO_2$ group was bonded, its coordination as a bidentate ligand involving one of the oxygen atoms, was possible. We had obtained Pd, [5] Pt, [6] and Rh [7] complexes involving such coordination of the 2-$C_6H_4NO_2$ group, but all attempts to prepare the related gold complexes were unsuccessful.

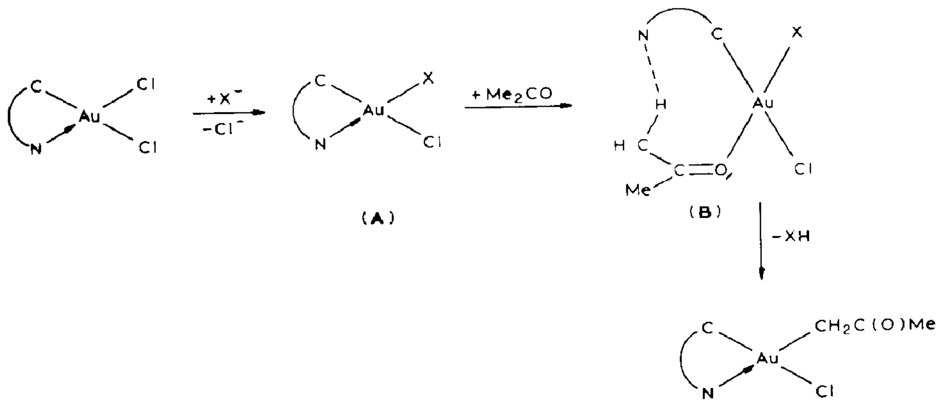
Results and discussion

Synthesis. The reaction between $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ and $[Hg(2\text{-}C_6H_4NO_2)_2]$ was studied under several conditions. A common feature was the presence of $(Me_4N)Cl$, our previous experience in transmetallation reactions using organomercury compounds having shown to us that this reagent has three main advantages. Firstly, the by-product of the transmetallation reaction, $[Hg(2\text{-}C_6H_4NO_2)Cl]$, undergoes symmetrization in the presence of Cl^- (eq. 3).

$$2[Hg(2\text{-}C_6H_4NO_2)Cl] + Cl^- \rightarrow [Hg(2\text{-}C_6H_4NO_2)_2] + [HgCl_3]^- \quad (3)$$

and this means that half as much of the $[Hg(2\text{-}C_6H_4NO_2)_2]$ complex has to be used. Secondly, the by-product of this last reaction $(Me_4N)[HgCl_3]$ is insoluble in dichloromethane, which is a good solvent for most aryl complexes; sometimes, as in the present case, $[Hg(2\text{-}C_6H_4NO_2)Cl]$ has a similar solubility to the product of the transmetallation reaction. Finally, $[Hg(2\text{-}C_6H_4NO_2)Cl]$ can be used as the starting material.

The complex $[Au(2\text{-}C_6H_4CH_2NMe_2)(2\text{-}C_6H_4NO_2)Cl]$ (I) can be obtained from $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ by treating it with $[Hg(2\text{-}C_6H_4NO_2)_2] + (Me_4N)Cl$



Scheme 1. Some steps in the suggested pathway for the reaction at a C–H band in acetone.

(2/1/1), or with $[Hg(2-C_6H_4NO_2)Cl] + (Me_4N)Cl$ (1/1/1) in refuxing ethanol, but the reaction is quite slow. When $[Hg(2-C_6H_4NO_2)_2]$ is used the reaction is complete in 15 h, but the yield is moderate (50%). When $[Hg(2-C_6H_4NO_2)Cl]$ is used about 80 h refluxing is required, but the yield is better (85%).

In acetone, when $[Hg(2-C_6H_4NO_2)Cl]$ and $(Me_4N)Cl$ are used, no reaction occurs in an hour at room temperature or 3 h under reflux. The complex $[Pd(2-C_6H_4NO_2)_2]$ also fails to react with $[\overline{Au(2-C_6H_4CH_2N}Me_2)Cl_2]$ in acetone in 24 h room temperature or in 9 h under reflux. In contrast $[\overline{Au(2-C_6H_4N=N}Ph)Cl_2]$ reacts with such reagents to give the product arising from C–H activation of the solvent $[\overline{Au(2-C_6H_4N=N}Ph)(CH_2C(O)CH_3)Cl]$ [1] (see Scheme 1). This difference in behaviour between $[\overline{Au(2-C_6H_4CH_2N}Me_2)Cl_2]$ and $[\overline{Au(2-C_6H_4N=N}Ph)Cl_2]$ in acetone is consistent with our proposed pathway for the C–H activation in which cleavage of the N–Au bond by acetone **A** → **B** is the first step after the substitution that gives **A**. Because such cleavage does not occur in complexes containing the ligand $2-C_6H_4CH_2NMe_2$ [9,14] the process is interrupted after substitution of the chloro ligand.

The low reactivity of $[Hg(2-C_6H_4NO_2)_2]$ in transfer of the aryl group to a gold centre has been previously observed. Thus, the reaction between $[AuCl_4]^-$ and $[Hg(2-C_6H_4NO_2)_2]$ requires 30 h refluxing in acetone [4], while $[\overline{Au(2-C_6H_4N=N}Ph)Cl_2]$ [8] or $[\overline{Au(2-C_6H_4CH_2N}Me_2)Cl_2]$ [9] are obtained in 24 h at room temperature from $[AuCl_4]^-$ and the corresponding organomercury compounds. Furthermore, the analogue of complex I, $[\overline{Au(2-C_6H_4CH_2N}Me_2)(Ph)Cl]$ was obtained from $[\overline{Au(2-C_6H_4CH_2N}Me_2)Cl_2]$ and $[HgPh_2]$ in 86% yield after 1 h at room temperature [2].

Complex I reacts with AgAc ($Ac = OOCCH_3$), KBr, or KI to give complexes $[\overline{Au(2-C_6H_4CH_2N}Me_2)(2-C_6H_4NO_2)X]$ (X = Ac (II), Br (III), I (IV)). The acetato complex II reacts with an equimolecular amount of HCl (aq.) to give I, which can be isolated analytically pure. The product of the transmetallation reaction is usually slightly contaminated, probably by colloidal gold because although the two products give identical ^1H NMR spectra, the percentage carbon found (34–35) is lower than the theoretical (36.9).

The reaction of I with PPh_3 (1/1) gives $[\overline{Au(2-C_6H_4CH_2N}Me_2)(2-C_6H_4NO_2)Cl(PPh_3)]$ (V). This behaviour contrasts with that of other related complexes. Thus, while the complex $[Au(2\text{-}C_6H_4CH_2NMe_2)(C_6F_5)Cl]$ does not react with PPh_3 [11], the analogous species $[Au(2\text{-}C_6H_4CH_2NMe_2)(R)Cl]$ ($R = 2\text{-}C_6H_4N{=}NPh$ [11], Ph [2]) do react, to give $[AuCl(PPh_3)]$ and the corresponding biphenyl. If the reaction between I and PPh_3 is carried out in 1/2 molar ratio, only a small amount of reduction to $[AuCl(PPh_3)]$ is found.

The cationic complex $[Au(2\text{-}C_6H_4CH_2NMe_2)(2\text{-}C_6H_4NO_2)(PPh_3)]ClO_4$ (VI) can be obtained by treatment of I with PPh_3 and $NaClO_4$ (1/1/1) or that of V with $NaClO_4$. Complex I does not react with pyridine or tetrahydrothiophene, even in the presence of $NaClO_4$.

To examine the possibility of coordination of the nitro group, the replacement of the chloro ligand in I by the labile ligand ClO_4^- was carried out by using $AgClO_4$ (1/1). However, the product was a very air-sensitive species, the IR spectrum of which suggested that there was coordination of the perchlorato ligand, and no nitro coordination (see below), which is consistent with our suggested sequence for the tendency of the nitro group to coordinate in 2-nitrophenylmetal complexes, namely $Au^{III} \ll Pt^{II} < Pd^{II} \ll Rh^{III} \gg Pt^{IV}$ [7]. Addition of excess of pyridine (py) to a dichloromethane solution of the perchlorato complex gave $[Au(2\text{-}C_6H_4CH_2NMe_2)(2\text{-}C_6H_4NO_2)(py)]ClO_4$ (VII), which could not be obtained by use of $NaClO_4$. The corresponding tetrahydrothiophene complex was also obtained, but was too unstable for full characterization. Table 1 shows the yields, elemental analyses, molar conductivities, and selected IR and NMR spectroscopic data.

IR and NMR spectra. Complexes I–VII all show a strong band at ca. 1330 cm^{-1} assignable to the $\nu_{sym}(NO_2)$ vibration mode, which means that the nitro group is not coordinated; such coordination causes this frequency to fall to ca. 1260 cm^{-1} [7]. The strong band at ca. 1500 cm^{-1} is assignable to $\nu_{asym}(NO_2)$ and is not sensitive to whether or not the nitro group is coordinated.

The ^1H NMR spectrum of complex I reveals that two isomers are present in chloroform solution. The ratio depends on the number of times the sample is recrystallized. It also depends on whether the complex is prepared by transmetallation or from complex II. The appearance of three singlets arising from the Me groups and an AB system (only clearly observable at 300 MHz) and a singlet arising from the CH_2 protons might be conceivably due to the presence of an isomer (**IA**) in which there is restricted rotation of the 2-nitrophenyl group, giving rise to inequivalence of both Me and CH_2 protons, along with another isomer (**IB**) in which these protons are equivalent because there is rotation or because there is coordination of the $2\text{-}C_6H_4NO_2$ group as a chelating ligand with the $2\text{-}C_6H_4CH_2NMe_2$ ligand monodentate rotating freely about the C–Au bond. In view of the low coordinating ability of the nitro group and the strong tendency of the $2\text{-}C_6H_4CH_2NMe_2$ group to act as a chelating ligand in gold(III) complexes the second possibility can be ruled out. The possibility that the second isomer could be the cationic complex $[Au(2\text{-}C_6H_4CH_2NMe_2)(2\text{-}C_6H_4NO_2)]Cl$ must also be ruled out because of the absence of conductivity in acetone.

From consideration of crystal structures of several $2\text{-}C_6H_4CH_2NMe_2$ gold(III) complexes [2,11,14,15], we suggest that the isomer having the two aryl groups in a *cis* disposition is **IB**, because with this geometry the 2-nitrophenyl group seems to have more freedom of rotation around the C–Au bond. In terms of this assignment the isomer **IA** would be that having the aryl groups *trans* to one another.

Complex I shows a strong band at 300 cm^{-1} assignable to the $\nu(AuCl)$ frequency.

Table 1

Analytical and other data for complexes I–VII

Compound	^{1}H NMR [a]	Λ_M [b]	Yield (%)	Analytical data (found (calc.) (%))			
				C	H	N	Au
[Au(2-$C_6H_4CH_2NMe_2$)(2-$C_6H_4NO_2$)Cl]	3.11 (Me), 3.14 (Me), 3.30 (Me)	0	40/85 [c]	36.3	3.2	5.4	39.7
(I)	4.21, 4.25 (CH_2, AB system, ^2J(HH) 14 Hz), 4.38 (CH_2)			(36.9)	(3.3)	(5.7)	(40.3)
[Au(2-$C_6H_4CH_2NMe_2$)(2-$C_6H_4NO_2$)(Ac)]	1.89 (MeCO), 2.14 (MeCO), 3.01 (MeN),	0	60	39.9	3.7	5.6	38.3
(II)	3.16 (MeCO), 4.15 (CH_2), 4.25 (CH_2)			(39.8)	(3.5)	(5.5)	(38.4)
[Au(2-$C_6H_4CH_2NMe_2$)(2-$C_6H_4NO_2$)Br]	3.15 (Me), 3.26 (Me),	0	75	33.0	3.1	4.9	36.5
(III)	4.21 (CH_2), 4.35 (CH_2)			(33.8)	(3.0)	(5.2)	(36.9)
[Au(2-$C_6H_4CH_2NMe_2$)(2-$C_6H_4NO_2$)I]		1.3	70	30.9	2.7	4.2	33.8
(IV)				(31.0)	(2.8)	(4.8)	(33.9)
[A(2-$C_6H_4CH_2NMe_2$)(2-$C_6H_4NO_2$)Cl(PPh_3)]	3.09 (Me), 3.11 (Me), 4.21 (CH_2)	17	75	52.0	4.3	3.4	26.5
(V)				(52.8)	(4.2)	(3.7)	(26.2)
[Au(2-$C_6H_4CH_2NMe_2$)(2-$C_6H_4NO_2$)(PPh_3)]ClO_4		134	83	48.4	4.0	3.9	24.3
(VI)				(48.6)	(3.8)	(3.4)	(24.1)
[Au(2-$C_6H_4CH_2NMe_2$)(2-$C_6H_4NO_2$)(py)]ClO_4		136	63	37.8	3.4	6.4	31.0
(VII)				(38.0)	(3.3)	(6.6)	(31.2)

[a] At 25 °C, TMS as reference, 80 MHz, except for complex I at 300 MHz. Except for the **AB** system in I all the signals are singlets. [b] In Ω^{-1} cm^2 mol^{-1} in acetone (ca. 5×10^{-4} $mol\times dm^{-3}$). [c] See text.

The position of this band coincides with that for the related complex [Au(2-$C_6H_4CH_2NMe_2$)(Ph)Cl] [2], the crystal structure of which shows the chloro ligand to be *trans* to the carbon atom of the chelating ligand, suggesting that this band belongs to the **IB** isomer. The other isomer should give a band at ca. 350 cm^{-1} [9], but although there is a weak absorption at 360 cm^{-1}, a band in this region is also observed for the other complexes. All attempts to grow single crystals of I failed.

Complexes II and III show a similar doubling of the resonances for the Me and CH_2 protons and, in addition, there are also two different resonances for the acetato ligand in the cases of II. Complexes IV and VII partially decompose in solution, preventing assignment of the NMR resonances.

The ^{31}P NMR spectrum of V shows that there is only one isomer in solution (δ 30.34 ppm). Given its low conductivity in acetone (Λ_M 17 Ω^{-1} cm^2 mol^{-1}), the complex could or could not be pentacoordinate, depending on the nature of the coordination of the 2-$C_6H_4CH_2NMe_2$ group. Since this ligand is chelating in all the gold(III) complexes we have structurally characterized [2,11,14,15] and the N–Au bond is resistant even to an excess of PPh_3 we, assume that V is pentacoordinate. We have prepared most of the pentacoordinated organogold(III) complexes reported [14]. Those characterized by X-ray diffraction have a distorted square-planar geometry. Complex VI is not soluble enough to allow recording of its NMR spectra.

Experimental

Recording of the IR spectra, the C, H and N analyses, and conductance measurements were performed as described previously [7]. NMR spectra (in $CDCl_3$) were recorded with Bruker AM300 and Varian FT80 spectrometers. Unless otherwise stated reactions were carried out at room temperature with magnetic stirring without special precautions to exclude light or moisture. The accounts below refer to the methods giving the best yields. Table 1 shows the yields, elemental analyses, molar conductivities, and selected IR and NMR data.

[Au(2-$C_6H_4CH_2NMe_2$)(2-$C_6H_4NO_2$)X] (X = Cl (I), Ac (II))

To an ethanol solution (30 cm^3) of [Au(2-$C_6H_4CH_2NMe_2$)Cl_2] [9] (181 mg, 0.44 mol) were added solid [Hg(2-$C_6H_4NO_2$)$_2$] [16] (100 mg, 0.22 mmol) and (Me_4N)Cl (48 mg, 0.44 mmol). After 65 h refluxing, the solvent was removed and the residue extracted with dichloromethane (3 × 5 cm^3). The suspension was filtered through $MgSO_4$ and the filtrate concentrated to ca. 1 cm^3. n-Hexane (15 cm^3) was added, to give a precipitate which was filtered off and recrystallized from dichloromethane/n-hexane (1/5) to give impure I (85% yield).

This impure I (60 mg, 0.12 mmol) was dissolved in acetone (10 cm^3) and solid AgAc (20 mg, 0.14 mmol) was added. The suspension was stirred for 36 h in the dark and work up as above gave II as a white solid.

To an acetone (10 cm^3) solution of II (80 mg, 0.16 mmol) was added 1.63 cm^3 of aqueous HCl (0.1 mmol/cm^3). After 4 h the solution was worked up as described for the transmetallation reaction to give pure I (40% yield).

[Au(2-$C_6H_4CH_2NMe_2$)(2-$C_6H_4NO_2$)X] (X = Br (III), I (IV))

To an acetone solution (10 cm^3) of crude I (100 mg, 0.2 mmol) was added an excess of KX (0.6 mmol). After 72 h the solvent was removed and the residue extracted with dichloromethane (3 × 5 cm^3). The suspension was filtered through $MgSO_4$ and the filtrate concentrated to ca. 1 cm^3. n-Hexane (15 cm^3) was added to give a precipitate of III (yellow) or IV (brown).

$[\overline{Au(2\text{-}C_6H_4CH_2N}Me_2)(2\text{-}C_6H_4NO_2)Cl(PPh_3)]$ (V)

To a dichloromethane solution (10 cm^3) of I (60 mg, 0.12 mmol) was added solid PPh_3 (32 mg, 0.12 mmol). After 1 h the yellow solution was concentrated to 1 cm^3 and n-hexane (10 cm^3) added slowly to precipitate V as a yellow solid.

$[\overline{Au(2\text{-}C_6H_4CH_2N}Me_2)(2\text{-}C_6H_4NO_2)(PPh_3)]ClO_4$ (VI)

To an acetone solution (10 cm^3) of crude I (100 mg, 0.2 mmol) were added solid PPh_3 (52 mg, 0.2 mmol) and $NaClO_4 \cdot H_2O$ (28 mg, 0.2 mmol). After 48 h the solvent was removed and the residue extracted with dichloromethane (3 × 5 cm^3). The suspension was filtered through $MgSO_4$, the filtrate concentrated to ca. 1 cm^3, and diethyl ether (15 cm^3) added to give a cream precipitate of VI.

$[\overline{Au(2\text{-}C_6H_4CH_2N}Me_2)(2\text{-}C_6H_4NO_2)(py)]ClO_4$ (VII)

To an acetone solution (10 cm^3) of crude I (50 mg, 0.1 mmol) was added solid $AgClO_4$ (21 mg, 0.1 mmol). After 10 min the solvent was removed and the residue extracted with dichloromethane (3 × 5 cm^3). The suspension was filtered through $MgSO_4$ and an excess of pyridine added to the filtrate. After 2 h the solution was concentrated to ca. 2 cm^3, and diethyl ether (10 cm^3) was added to give precipitate of VII.

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