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Attempts to prepare mixed diarylgold(III) complexes containing a pentafluorophenyl group. Synthesis of [2-{(dimethylamino)-methyl}phenyl-C^1N)-(pentafluorophenyl)gold(III) complexes

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Abstract

$[Hg(C_6F_5)_2]$ reacts (1/1) with $(PhCH_2PPh_3)$ $[AuCl_2]$ or with (Me_4N) $[AuCl_4]$ to give $(PhCH_2PPh_3)$ $[Au(C_6F_5)Cl]$ (**1**) or (Me_4N) $[Au(C_6F_5)Cl_3]$ (**2b**), respectively. Complex **1** reacts with chlorine to give $(PhCH_2PPh_3)$ $[Au(C_6F_5)Cl_3]$ (**2a**). $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ reacts with $AgOOCC_6F_5$ (1/2) to give $[Au(2\text{-}C_6H_4CH_2NMe_2)(OOCC_6F_5)_2]$ (**3**), which does not undergo decarboxylation when heated as a solid in the range 30–400 °C. The reaction of $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ with $[Hg(C_6F_5)_2]$ and $(Me_4N)Cl$ (2/1/2) affords $[Au(2\text{-}C_6H_4CH_2NMe_2)(C_6F_5)Cl]$ (**4**) which reacts with KBr or AgO_2CMe to give $[Au(2\text{-}C_6H_4CH_2NMe_2)(C_6F_5)X]$ ($X = Br$ (**5**), O_2CMe (**6**)) and with pyridine (py) in the presence of $NaClO_4$ to give the cationic species $[Au(2\text{-}C_6H_4CH_2NMe_2)(C_6F_5)(py)]ClO_4$ (**7**).

Introduction

When we reported [1g] the synthesis of organogold(I) complexes of formula $[Au(R)Cl]^-$ ($R = 2$-, 3-, $4\text{-}C_6H_4NO_2$) by the transmetallation reaction $[AuCl_2]^- + [HgR_2] \rightarrow [Au(R)Cl]^- + [Hg(R)Cl]$ the only examples of such type of complexes were pentafluorophenyl derivatives obtained [2] by the following two-step sequence:

$$[AuCl(tht)] + RLi \longrightarrow [Au(R)(tht)] \xrightarrow{+Cl^-} [Au(R)Cl]^-$$

$(R = C_6F_5$; tht = tetrahydrothiophene)

The synthetic interest of the new method was based not only on the fact that it was a one-step process but also on the fact that it does not require an inert atmosphere and the advantage of the much greater availability of $[HgR_2]$ than of RLi compounds. However, in order to define the scope of the organomercury route we decided to extend it to other R groups, and first examined C_6F_5, the only one for which the comparison with the other method is appropriate.

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We have also reported the use of arylmercury compounds to prepare mono- and di-(homo and hetero) arylcomplexes [1,3]. Owing to the scarcity of the mixed diarylgold(III) complexes [4] we thought it of interest to extend the method to the synthesis of C_6F_5 complexes, of which only *trans*-$[Au(C_6F_5)(2,4,6\text{-}C_6F_3H_2)X_2]^-$ with X = Br or I had been reported previously [2c].

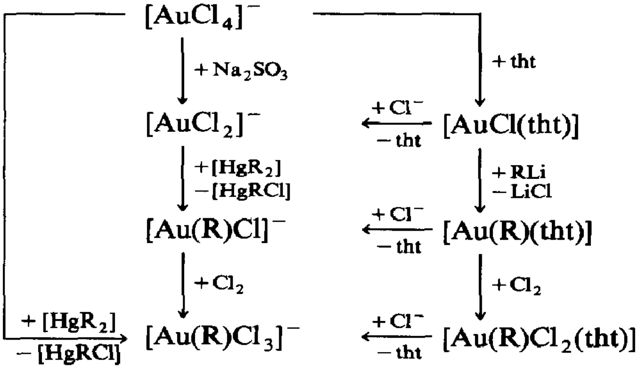
Results and discussion

$(PhCH_2PPh_3)[AuCl_2]$ reacts with $[Hg(C_6F_5)_2]$ (1/1, CH_2Cl_2) to give $(PhCH_2PPh_3)[Au(C_6F_5)Cl]$ (**1**). The process is slow, not being complete after 2 h at room temperature in dichloromethane or after 5 h refluxing in acetone. After 80 h at room temperature in dichloromethane the only isolable products were **1** and the by-product $[Hg(C_6F_5)Cl]$. Complex **1** was previously synthesized [2d] by treating $[Au(C_6F_5)(tht)]$ with $(PhCH_2PPh_3)Cl$. The overall yield from the starting complex [AuCl(tht)] (70%) was similar to that in the present method (75%).

There are two possible ways of preparing mixed pentafluorophenylarylgold(III) complexes and the choice depends on the relative order with which the aryl groups are transferred to the gold centre. In our experience anionic complexes are the best for transmetallation reactions, and so $[Au(C_6F_5)Cl_3]^-$ should be the most convenient starting complex for the second arylation reaction if the C_6F_5 group is to be attached first. There were two possible ways of making it: (i) by oxidation of complex **1** with chlorine, which is a known process, and (ii) by a transmetallation reaction between $[Hg(C_6F_5)_2]$ and $[AuCl_4]^-$ (1/1), which had never previously been tried. As expected, $(PhCH_2PPh_3)[Au(C_6F_5)Cl_3]$ (**2a**) was obtained by treating **1** with an excess of a solution of chlorine in CCl_4; this method had previously been used [2] to prepare $(n\text{-}Bu_4N)[Au(C_6F_5)Br_3]$ from $(n\text{-}Bu_4N)[Au(C_6F_5)Br]$.

Our previous experience has shown that transmetallation reactions between $[HgR_2]$ and $[AuCl_4]^-$ (1/1) can give either a monoaryl complex, as is the case when $R = 2\text{-}C_6H_4N{=}NPh$ or $2\text{-}C_6H_4CH_2NMe_2$, or a diaryl complex, even when a 1/1 molar ratio is used as is the case when $R = 2\text{-}C_6H_4NO_2$ or $C_6H_3\text{-}2\text{-}Me\text{-}6\text{-}NO_2$.

The reaction between $[Hg(C_6F_5)_2]$ and $(Me_4N)[AuCl_4]$ (1/1) gives $(Me_4N)[Au(C_6F_5)Cl_3]$ (**2b**) in high yield (81%). This reaction does not occur at room temperature but is complete after 18 h refluxing in acetone. The method is more convenient than that involving chlorine oxidation, and much more convenient than the reported four step synthesis of **2a** (from $[AuCl_4]^-$) [5]. Scheme 1 summarizes the various methods described here and previously [2,4,5] for making complexes $[Au(R)Cl]^-$ or $[Au(R)Cl_3]^-$ ($R = C_6F_5$).



Scheme 1. Outline of the various ways of preparing complexes $[Au(R)Cl^-$ or $[Au(R)Cl_3]^-$ ($R = C_6F_5$).

Attempted transmetallations between **2a**, **b** and $[HgR_2]$ ($R = 2\text{-}C_6H_4CH_2NMe_2$ or $2\text{-}C_6H_4N{=}NC_6H_5$ in acetone at room temperature; $R = Ph$, in refluxing acetone) led to decomposition to metallic gold. However, reaction of **2b** with $[Hg(2\text{-}C_6H_5NO_2)_2]$ gave a compound which appeared from its IR spectrum to be $(Me_4N)[Au(C_6F_5)(2\text{-}C_6H_5NO_2)Cl_2]$, but which we were unable to isolate analytically pure.

We tried two other ways of preparing mixed diarylgold(III) complexes containing one C_6F_5 group. Both were designed to give complexes with the $2\text{-}C_6H_4CH_2NMe_2$ group as the second aryl ligand. First we tried to prepare $[Au(2\text{-}C_6H_4CH_2NMe_2)(C_6F_5)_2]$ by decarboxylation of $[Au(2\text{-}C_6H_4CH_2NMe_2)(OOCC_6F_5)_2]$ (**3**), which was itself obtained by treating $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ with $AgOOCC_6F_5$ (1/2). However, thermal gravimetric analysis of **3** over the range 30 to 400 °C revealed no weight loss corresponding to one or two CO_2 molecules, and so no C_6F_5-gold complexes could be obtained in this way. At 257 °C the whole organic content was lost, to give a residue corresponding to the amount of gold in the sample.

The other attempt involved a transmetallation reaction between $[Hg(C_6F_5)_2]$ and $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ (1/1 ratio in refluxing xylene for 8 h) which gave a mixture of $[Au(2\text{-}C_6H_4CH_2NMe_2)(C_6F_5)Cl]$ and $[Hg(C_6F_5)Cl]$. The very similar solubilities of these two products made it impossible to separate them.

The complex $[Au(2\text{-}C_6H_4CH_2NMe_2)(C_6F_5)Cl]$ (**4**) was finally isolated from the reaction of $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ with $[Hg(C_6F_5)_2]$ (2/1 ratio in refluxing xylene) in the presence of an excess of Me_4NCl. The presence of this salt promotes the symmetrization of the mercury by-product, reducing by 50% the amount of $[Hg(C_6F_5)_2]$ required, and producing the insoluble salt $(Me_4N)_2[Hg_2Cl_6]$, which is readily separated from complex **4**.

$$[Hg(C_6F_5)Cl] + 1/2Cl^- \longrightarrow 1/2[Hg(C_6F_5)_2] + 1/4[Hg_2Cl_6]^{2-}$$

However, owing to extensive decomposition to metallic gold the yield was only moderate (41%).

A similar reaction between $[Au(2\text{-}C_6H_4N{=}NPh)Cl_2]$ and $[Hg(C_6F_5)_2]$ in refluxing xylene gave metallic gold, whereas the room temperature reaction in acetone of $[Au(2\text{-}C_6H_4N{=}NPh)Cl_2]$ and $[Hg(C_6F_5)_2]$ in the presence of Me_4NCl (2/1/2) gave the acetonyl complex $[Au(2\text{-}C_6H_4N{=}NPh)(CH_2COCH_3)Cl]$ [1n].

Complex **4** reacted with AgO_2CMe (1/1) or KBr (excess) to give $[Au(2\text{-}C_6H_4CH_2NMe_2)(C_6F_5)X]$ ($X = O_2CMe$ (**5**), Br (**6**)). The reaction of **4** with $NaClO_4$ (1/1) and an excess of pyridine gave the cationic species $[Au(2\text{-}C_6H_4CH_2NMe_2)(C_6F_5)(py)]ClO_4$ (**7**).

The C–Au and N–Au bonds in complex **4** are remarkably strong. Thus, **4** does not react with Me_4NCl or PPh_3 (1/1 ratio in refluxing acetone for 8 h), in contrast with the behaviour of other diarylgold(III) complexes. Thus, $[Au(2\text{-}C_6H_4\text{-}N{=}NPh)_2Cl]$ reacts with Cl^- or PPh_3 to give the gold(I) complexes $[AuCl_2]^-$ or $[AuCl(PPh_3)]$, respectively. A similar result is obtained when $[Au(2\text{-}C_6H_4CH_2NMe_2)(Ph)Cl]$ or $[Au(2\text{-}C_6H_4CH_2NMe_2)(2\text{-}C_6H_4N{=}NPh)Cl]$ is treated with PPh_3 [1h, f, m]. Complex **4** is also inert towards the bidentate ligand 1,10-phenantroline (1/1 ratio in CH_2Cl_2 at room temperature) even in the presence of $NaClO_4$.

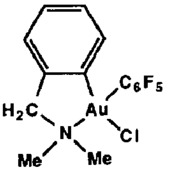


Fig. 1. Suggested structure of complex **4**.

IR spectra

The new gold complexes **2b**–**7** show bands characteristic of the C_6F_5 group at 1500, 1070, 960 and 800 cm^{-1}. Complex **3** also shows two bands of medium intensity at 820 and 810 cm^{-1}, as expected for the presence of two *cis*-$OOCC_6F_5$ groups. This species also shows bands assignable to $\nu_{asym}(CO_2)$ at 1680 and 1660 cm^{-1}.

The IR spectrum of the bromo complex **6** is identical to that of **4** except for the presence in the case of **4** of a band at 318 cm^{-1} (s) assignable to ν(AuCl), and the presence in the case of **6** of a weak band at 225 cm^{-1}, assignable [6] to ν(AuBr). The position of the ν(AuCl) band in **4** is consistent with the chloro being *trans* to the phenyl group of the 2-$C_6H_4CH_2NMe_2$ ligand [1e, m] (see Fig. 1); thus the two aryl groups are mutually *cis* as was been found [im] by a X-ray diffraction study in the case of the related complex [Au(2-$C_6H_4CH_2NMe_2$)(Ph)Cl]. Complex **5** shows bands at 1635 vs and 1310 vs cm^{-1} assignable to $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$, respectively. The positions of these bands indicate that the acetatoxy group occupies a similar position to that of the chloro ligand in **4** [1f, j].

The cationic species **7** shows the expected bands for the pyridine ligand (1600 cm^{-1}) and the ClO_4^- group (1080 and 620 cm^{-1}).

NMR spectra

In order to confirm the presence of both 2-$C_6H_4CH_2NMe_2$ and C_6F_5 groups, the ^1H and ^{19}F NMR spectra were recorded for complexes **4** and **6**. ^1H NMR spectra show singlets in a 3/1 ratio for methyl and methylene groups [3.13 and 4.30 ppm (**4**); 3.18 and 4.37 ppm (**6**)], while aromatic protons give as multiplets [7.16–7.26 ppm (**4**) and 6.36–7.21 ppm (**6**)]. The ^{19}F spectra show the expected resonances for a C_6F_5 group. The resonances (with respect to $CFCl_3$) corresponding to *para*-F appear as a triplet in both complexes with $J(FF) = 20$ Hz [-149.3 ppm (**4**); -148.9 ppm (**6**)], while those from the *ortho*- [-113.7 ppm (**4**); -114.0 ppm (**6**)] and *meta*-F [-154.3 ppm (**4**); -154.0 ppm (**6**)] appear as multiplets.

Experimental

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin–Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 10^{-4} mol dm^{-3} acetone solutions with a Philips 9501 conductimeter and molar conductivities (Λ_M) are given in Ω^{-1} cm^2 mol^{-1}. 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. Thermogravimetric examination of complex **3** was performed with a Mettler TA3000 apparatus. Reactions were carried out at room temperature with magnetic stirring and without special precautions against light or moisture unless otherwise state. The starting complexes $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ and $[Hg(C_6F_5)_2]$ were prepared by published methods [1e,7]. $AgOOCC_6F_5$ was made by treating C_6F_5COOH with Ag_2CO_3 (2/1 ratio in acetone, at room temperature for 24 h). The ^1H and ^{19}F NMR spectra were recorded in $CDCl_3$ solutions (δ in ppm with respect to TMS or $CFCl_3$) on a Varian FT-80 spectrometer. The complexes are colourless unless otherwise stated.

$(PhCH_2PPh_3)[Au(C_6F_5)Cl]$ (1)

To a solution of $(PhCH_2PPh_3)[AuCl_2]$ (118 mg, 0.20 mmol) in CH_2Cl_2 (10 cm^3) was added solid $[Hg(C_6F_5)_2]$ (100 mg, 0.20 mmol). After 96 h the solvent was removed under vacuum to ca. 0.5 cm^3 and diethyl ether (10 cm^3) added. The precipitate of **1** was recrystallized from CH_2Cl_2/Et_2O (1/10) (75% yield; m.p. 145 °C, lit. 144 °C [2d]). $\Lambda_M = 104$. IR $\nu(AuCl)$ 320 cm^{-1}. Analytical data. Found: C, 50.39; H, 3.22; Au, 25.43. $C_{31}H_{22}AuClF_5P$ calc: C, 49.45; H. 2.95; Au, 26.16%.

$(PhCH_2PPh_3)[Au(C_6F_5)Cl_3]$ (2a)

To a solution of **1** (124 mg, 0.17 mmol) in CH_2Cl_2 (10 cm^3) was added an excess of Cl_2 in CCl_4. After 1 h the yellow solution was concentrated to ca. 1 cm^3. Addition of Et_2O (10 cm^3) gave a pale yellow precipitate of **2a**, which was recrystallized from CH_2Cl_2/Et_2O (1/5) (82% yield; m.p. 187 °C, lit. 205(d) °C [5]). $\Lambda_M = 113$. IR, $\nu(AuCl)$ 358m, 359w, 310m cm^{-1}. Analytical data. Found: C, 45.49; H, 2.97; Au, 24.02. $C_{31}H_{22}AuCl_3F_5P$ calc: C, 45.20; H, 2.69; Au, 23.91%.

$(Me_4N)[Au(C_6F_5)Cl_3]$ (2b)

To a solution of $(Me_4N)[AuCl_4]$ (300 mg, 0.73 mmol) in acetone (30 cm^3) was added solid $[Hg(C_6F_5)_2]$ (390 mg, 0.73 mmol). The mixture was refluxed for 18 h and the solvent then evaporated to ca. 1 cm^3. Diethyl ether (20 cm^3) was added to give a precipitate of a pale yellow solid **2b** (81% yield; m.p. 198 °C). $\Lambda_M = 137.5$. IR $\nu(AuCl)$ 355, 310 cm^{-1}. Analytical data. Found: C, 22.08; H, 2.13; N, 2.49; Au, 36.02. $C_{10}H_{12}NAuCl_3F_5$ calc: C, 22.06; H, 2.22; N, 2.57; Au, 36.17%.

$[Au(2\text{-}C_6H_4CH_2NMe_2)(OOCC_6F_5)_2]$ (3)

To a solution of $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$(50 mg, 0.12 mmol) in acetone (15 cm^3) was added solid $AgOOCC_6F_5$ (80 mg, 0.25 mmol). After 2 h the solvent was evaporated and the residue extracted with CH_2Cl_2 (3×5 cm^3). The extract was filtered through $MgSO_4$ and concentrated to ca. 1 cm^3. Addition of diethyl ether (10 cm^3) gave **3** (50% yield; m.p. 153 °C dec.). $\Lambda_M = 0$. IR $\nu_{asym}(CO_2)$ 1685, 1660 cm^{-1}. Analytical data. Found: C, 36.77; H, 2.11; N, 1.90; Au, 26.42. $C_{23}H_{12}NAuF_{10}O_4$ calc: C, 36.67; H, 1.61; N, 1.86; Au, 26.15%.

$[Au(2\text{-}C_6H_4CH_2NMe_2)(C_6F_5)Cl]$ (4)

To a suspension of $[Au(2\text{-}C_6H_4CH_2NMe_2)Cl_2]$ (140 mg, 0.34 mmol) in xylene (10 cm^3) were added solid $[Hg(C_6F_5)_2]$ (92 mg, 0.17 mmol) and Me_4NCl (37 mg, 0.34 mmol). After 21 h refluxing the solvent was removed to dryness, the residue extracted with CH_2Cl_2 (3×5 cm^3) and the extract filtered through $MgSO_4$. Addition of n-hexane (1/5) gave microcrystals of **4** (41% yield; m.p. 187 °C). $\Lambda_M = 0$.

IR ν(AuCl) 318 cm^{-1}. ^{1}H NMR: 3.13(s, 6H); 4.30 (s, 2H); 7.16–7.23 (m, 4H); ^{19}F NMR: -154.3 (m, *meta*-F); -149.3 (t, *para*-F, J(FF) 20 Hz); -113.7 (m, *ortho*-F). Analytical data. Found: C, 34.72; H, 2.41; N, 2.78; Au, 36.66. $C_{15}H_{12}NAuClF_5$ calc: C, 33.76; H, 2.27; N, 2.62; Au, 36.91%.

$[A\overline{u(2\text{-}C_6H_4CH_2N}Me_2)(C_6F_5)(OOCCH_3)]$ *(5)*

To a solution of **4** (80 mg, 0.15 mmol) in acetone (10 cm^3) was added solid AgO_2CMe (25 mg, 0.15 mmol). The mixture was kept for 6 h in the dark, and the solvent was then removed. The residue was extracted with CH_2Cl_2 (3×5 cm^3) and the extract filtered through $MgSO_4$. Concentration of the solvent to ca. 1 cm^3 and addition of n-hexane (15 cm^3) gave a precipitate of **5** (65% yield; m.p. 163°C). $\Lambda_M = 0$. IR $\nu_{asym}(CO_2)$ 1635 cm^{-1}. Analytical data. Found: C, 36.48; H, 3.01; N, 2.27; Au, 34.82. $C_{17}H_{15}NAuF_5O_2$ calc: C, 36.64; H, 2.27; N, 2.51; Au, 35.32%.

$[A\overline{u(2\text{-}C_6H_4CH_2N}Me_2)(C_6F_5)Br]$ *(6)*

To a solution of **4** (76 mg, 0.14 mmol) in acetone (10 cm^3) was added solid KBr (60 mg, 0.51 mmol). After 70 h, work-up as for **5** and addition of diethyl ether (10 cm^3) gave **6** (95% yield; m.p. 151°C). $\Lambda_M = 0$. ^{1}H NMR: 3.18 (s, 6H); 4.37 (s, 2H); 6.36–7.21 (m, 4H). ^{19}F NMR: -154.0 (m, *meta*-F); -148.9 (t, *para*-F; J_{FF} 20Hz); -114.0 (m, *ortho*-F). Analytical data. Found: C, 31.62; H, 2.10; N, 2.58; Au, 34.31. $C_{15}H_{12}NAuBrF_5$ calc: C, 31.16; H, 2.09; N, 2.42; Au, 34.07%.

$[A\overline{u(2\text{-}C_6H_4CH_2N}Me_2)(C_6F_5)(py)]ClO_4$ *(7)*

To a solution of **4** (80 mg, 0.15 mmol) in acetone (10 cm^3) was added solid $NaClO_4$ (21 mg, 0.15 mmol) and an excess of pyridine. After 4 h, work-up as for **5** gave **7** (70% yield; m.p. 135°C) $\Lambda_M = 105$. Analytical data. Found: C, 36.25; H, 2.78; N, 4.20; Au, 28.90. $C_{20}H_{17}N_2AuClF_5O_4$ calc: C, 35.49; H, 2.53; N, 4.14; Au, 29.10%.

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