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Preliminary Communication

Gold in organic synthesis
Part 2*. Preparation of benzyl-alkyl and -arylketones via C–C coupling

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Abstract

Reaction of $[Au(\eta^2\text{-}Ar)\{CH_2C(O)R\}Cl]$ (Ar = $C_6H_4N{=}N$-Ph-2, R = Me, $C_6H_2(OMe)_3$-3′,4′,5′; Ar = $C_6H_3(N{=}NC_6H_4Me$-4′)-2, Me-5, R = Me) with PPh_3 and $NaClO_4 \cdot H_2O$ (1:2:1) at room temperature, leads to reductive elimination giving $[Au(PPh_3)_2]ClO_4$ and the corresponding carbon–carbon coupling product $ArCH_2C(O)R$. A similar process takes place when complexes $[Au(\eta^2\text{-}Ar)\{CH_2C(O)R\}(PPh_3)Cl]$ are refluxed in tetrahydrofuran, through elimination of $[Au(PPh_3)Cl]$.

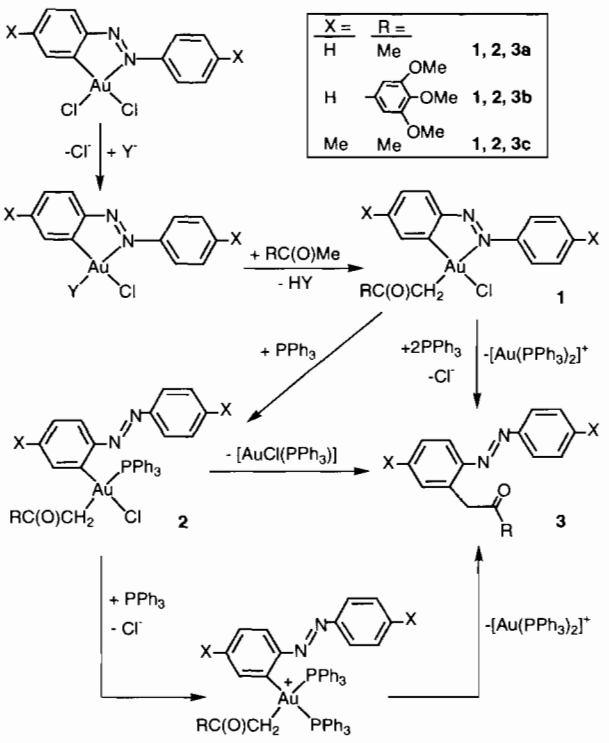
Key words: Coupling reaction; Ketones; Gold complexes; Phosphine complexes

Introduction

Thermolysis of alkyl–, alkylaryl–, alkyl(alkoxycarbonyl)– and vinyl–gold(III) complexes has been shown to give carbon–carbon coupling products [1]. We have previously reported the synthesis of symmetrical and unsymmetrical biaryls in mild conditions via C–C coupling by addition of PPh_3 to *cis*-diarylgold(III) complexes [2a]. Later, the same method was used in the demetallation of (η^3-butadienyl)palladium complexes [2b]. η^1- and η^3-allyl (acetylacetonato)–palladium and –platinum complexes also underwent reductive C–C coupling on treatment with excess PR_3 [2c]. We now report two different synthetic methods based on a similar behaviour of arylketonylgold(III) complexes which represent a new method of preparing benzyl-alkyl and -arylketones. We have obtained these gold(III) complexes as the products of the C–H activation of different ketones by 2-(phenylazo)phenylgold(III) complexes (see Scheme 1) [3].

Results and discussion

We have recently reported that $[Au(\eta^2\text{-}C_6H_4N{=}NPh\text{-}2)\{CH_2C(O)Me\}Cl]$ (**1a**) reacts with PPh_3 to give $[Au(C_6H_4N{=}NPh\text{-}2)\{CH_2C(O)Me\}Cl(PPh_3)]$ (**2a**). In solution, **2a** slowly undergoes reductive elimination to $[Au(PPh_3)Cl]$ and, presumably, the coupling product of the arylazoaryl and acetonyl groups **3a** (see Scheme 1) [3d]. We have confirmed this assumption and found other methods to prepare **3a**. Thus, addition of PPh_3 and $NaClO_4$ to **2a** (1:1:1) leads to C–C coupling to give **3a** and the reductive elimination product $[Au(PPh_3)_2]ClO_4$ (see Scheme 1). From a preparative point of view, quantitative yields of **3a** can be obtained: (i) by refluxing **2a** in THF (method a, see 'Experimental')



Y = ClO_4, acac

Scheme 1.

*For Part 1 see ref. 2a.
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or (ii) by addition of PPh_3 and $NaClO_4$ to **1a** in a 2:1:1 ratio in acetone at room temperature (method b) (see Scheme 1).

We have extended this study to the synthesis of new benzyl-alkyl and -arylketones using the above described methods, a and b, from a series of arylketonyl gold(III) complexes of general formula $[Au(\eta^2\text{-}Ar)\{CH_2C(O)R\}Cl]$ ($Ar = C_6H_4N{=}NPh$-2, $R = C_6H_2(OMe)_3$-3,4,5 (**1b**); $Ar = C_6H_3(N{=}NC_6H_4Me\text{-}4')$-2, Me-5, R = Me (**1c**)) or $[Au(Ar)\{CH_2C(O)R\}Cl(PPh_3)]$ ($Ar = C_6H_4N{=}NPh$-2, $R = C_6H_2(OMe)_3$-3,4,5 (**2b**); $Ar = C_6H_3(N{=}NC_6H_4Me\text{-}4')$-2, Me-5, R = Me (**2c**)) where Ar is *o*-metallated azobenzene or alkyldisubstituted azobenzenes and R is an alkyl or aryl group. Quantitative yields of ketones $ArCH_2C(O)R$ ($Ar = C_6H_4N{=}NPh$-2, $R = C_6H_2(OMe)_3$-3,4,5 (**3b**); $Ar = C_6H_3(N{=}NC_6H_4Me\text{-}4')$-2, Me-5, R = Me (**3c**)) were also obtained using both methods except for **2b** when method b was used (34%). In all cases, after the reductive elimination reactions, the solvent was removed and the residue was chromatographed through an alumina column eluting with n-hexane.

According to spectroscopic and X-ray diffraction studies complexes **1** and **2** have the structures depicted in Scheme 1 [3]. Complexes **2** are unstable because of the coordination of PPh_3 *trans* to the $CH_2C(O)R$ group, according to the antisymbiotic effect [4]. The same is applicable to the expected products of the reaction of **2** and PPh_3 which should be less stable.

One interesting feature of the synthetic methods presented here is the possibility of recycling gold from the gold(I) byproducts following the method previously described by us [2a]. We are now studying the possibility of a more direct synthesis of complexes **1** by reacting $[Hg(Ar)_2]$ with $Me_4N[AuCl_4]$ (1:1) in the corresponding ketone as solvent, but in the case of Ar = 2-phenylazophenyl and R = Me, the process takes place with decomposition to metallic gold and the yield of **1a** is very low. The requirement of Ar having an azo group, imposed by the method of synthesis of complexes **1** (see Scheme 1), reduces the synthetic utility of the method. However, we plan in the near future to overcome this limitating factor by looking for different methods to coordinate the ketonyl group to other aryl-gold(III) complexes. The use of other metals (for example, palladium) will also be tested.

All ketones **3** show the $\nu(CO)$ mode at higher frequencies (30–40 cm^{-1}) than that in the corresponding gold complexes.

Conclusions

Taking advantage of the instability of complexes of the type *cis*-$[Au(R)(R')Cl(PPh_3)]$ and *cis*-$[Au(R)(R')(PPh_3)_2]^+$, we have designed a method that allows us to prepare the C–C coupling products R-R', where R = azophenyl and $R' = CH_2C(O)R''$. This method has obvious possibilities to be extended to other R and R' groups.

Experimental

NMR spectra were carried out in $CDCl_3$ solutions (data are given in ppm with TMS as a reference, see footnotes). The starting gold complexes were prepared as described in ref. 3.

Preparation of the benzyl-alkyl and benzyl-arylketones

Method a. $[Au(Ar)\{CH_2C(O)R\}(PPh_3)Cl]$ (0.10 mmol) was dissolved in THF (50 cm^3) and stirred under reflux for 24 h. The solvent was removed to dryness and n-hexane (50 cm^3) added to give a suspension that was filtered to give a white solid, $[Au(PPh_3)Cl]$ (0.10 mmol), and a red solution that was concentrated *in vacuo* to give an orange residue that was chromatographed through alumina (2×15 cm, n-hexane as eluent). Removal of the solvent yielded orange solids. Yield (%): 95 (**1**), 98 (**2**), 85 (**3**)*.

Method b. To an acetone solution of $[Au(\eta^2\text{-}Ar)\{CH_2C(O)R\}Cl]$ (0.10 mmol), solid PPh_3 (0.20 mmol) and $NaClO_4 \cdot H_2O$ (0.10 mmol) were added and the mixture stirred at room temperature for 48 h. Removal of the solvent and addition of n-hexane afforded a white solid, $[Au(PPh_3)_2]ClO_4$ (0.10 mmol), and a red solution. Workup as above yielded orange solids. Yield (%): 98 (**1**); 34 (**2**); 81 (**3**).

*M.p. (°C): 72 (**3a**), 96 (**3b**), 116 (**3c**). MS (*m/e*): **3a**: 238 (M^+, 1%), 222 (13%), 195 (100%), 105 (PhN_2, 20%), 77 (Ph, 54%), 51 (C_4H_3, 17%); **3b**: 390 (M^+, 1%), 195 (100%), 77 (Ph, 51%), 51 (C_4H_3, 11%); **3c**: 266 (M^+, 1%), 223 (80%), 152 (24%), 119 (14%), 91 (33%), 77 (Ph, 57%), 51 (C_4H_3, 30%). ^1H NMR: **3a**: 2.2 (s, 3H, Me), 4.2 (s, 2H, CH_2), 7.3–7.9 (m, 9H, arylic protons); **3b**: 3.7 (s, 6H, OMe), 3.9 (s, 3H, OMe), 4.8 (s, 2H, CH_2), 7.3–7.7 (m, 11H, arylic protons); **3c**: 2.3 (s, 3H, MeCO), 2.4 (s, 3H, MeC_6H_4), 2.5 (s, 3H, MeC_6H_4), 4.2 (s, 2H, CH_2), 7.3–7.5 (m, 7H, arylic protons). ^{13}C NMR: **3a**: 29.3 (Me), 46.9 (CH_2), 116.1, 123.1, 128.1, 129.2, 131.2, 131.5, 131.7, 135.1 (arylic carbons), 150.1 (C–N), 152.9 (C–N), 206.3 (CO); **3b**: 41.2 (CH_2), 56.3 [2(OMe)], 60.9 (OMe), 105.9, 115.9, 123.2, 128.5, 130.1, 131.3, 132.0, 135.9, 138.9, 140.4, 142.5, 149.7, 150.7, 153.1 (arylic carbons), 196.9 (CO); **3c**: 21.5 (MeCO), 21.6 (MeC_6H_4), 47.0 (CH_2), 116.0, 122.9, 128.7, 129.4, 129.9, 131.9, 132.1, 132.2 (arylic carbons), 146.7 (C–N), 148.3 (C–N), 204.1 (CO). *Anal.* Calc. for $C_{15}H_{14}N_2O$ (**3a**): C, 75.6; H, 5.9; N, 11.8. Found: C, 74.9; H, 6.1; N, 11.4%. Calc. for $C_{23}H_{22}N_2O_4$ (**3b**): C, 70.8; H, 5.7; N, 7.2. Found: C, 69.9; H, 5.9; N, 6.8%. Calc. for $C_{17}H_{18}N_2O$ (**3c**): C, 76.7; H, 6.8; N, 10.5. Found: 76.3; H, 7.0; N, 10.2%.

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