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Transfer of organic groups to gold using organotin compounds

Nadine Meyer, Sivatharushan Sivanathan, Fabian Mohr *

Fachbereich C - Anorganische Chemie, Bergische Universität Wuppertal, 42119 Wuppertal, Germany

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ABSTRACT

$PhSnMe_3$ undergoes transmetallation with $[AuCl(EPh_3)]$ (E = P, As) in refluxing toluene forming $[AuPh(EPh_3)]$ and Me_3SnCl. The analogous ^{n}Bu derivative does not transmetallate, even under forcing conditions. Similarly, 1-(trimethylstannyl)naphthalene and 1-(trimethylstannyl)-8-iodonaphthalene react with $[AuCl(PPh_3)]$ to give good yields of the corresponding naphthylgold(I) complexes which were spectroscopically and structurally characterised.

1. Introduction

Traditionally, organolithium compounds or Grignard reagents are used as transmetallating agents in the synthesis of organogold compounds [1–3]. Especially reactions involving organolithium species tend to cause problems with gold precursors, as the reducing properties of the organolithiums lead to formation of metallic gold thus lowering yields. Furthermore, organolithium compounds and Grignard reagents are not compatible with several functional groups and also require rigorous exclusion of moisture and air. From the late 1970's Eaborn and Pidcock published a series of papers in which the use of organotin compounds as aryl-transfer agents to various platinum precursors under mild conditions was described [4–10]. Some years later the group of Brune used the same approach to transfer various naphthyl derivatives to a platinum(II) centre [11–13]. It was also shown that organotin reagents can transfer organic groups to palladium, although not always the desired aryl unit was transferred [14,15]. There is also precedence for the use of an organotin compound as transmetallating agent in gold(III) chemistry (Fig. 1) [16]. One report also details the transfer of a metal-alkyne unit *via* the tin compound to a gold(I) centre (as an example an iron derivative is shown in Fig. 1) [17]. Based on these results, we wondered if readily accessible and air- and moisture-stable aryltin compounds would also undergo transmetallation with gold(I) species. Indeed, we recently communicated that 1,8-bis(trimethylstannyl)naphthalene readily transfers the 1,8-naphthalenediyl unit to a dinuclear gold(I) centre in good yields under mild conditions (Fig. 1) [18]. It should be mentioned here, that boronic acids have also been used to transfer aryl groups to gold under reasonably mild but albeit time consuming conditions (^{i}PrOH reflux for a minimum of 24 h) [19–21].

Herein we report further results of reactions of aryltin compounds with gold(I) precursors to learn more about the scope and generality of this process. Furthermore, we report the successful transmetallation of a halide-functionalised aryltin compound to a gold(I) centre, something which is not possible using organolithium species or Grignard reagents.

2. Results and discussion

Initially we examined the reaction of $PhSnMe_3$ and $PhSn^nBu_3$ with $[AuCl(PPh_3)]$ and $[AuCl(AsPh_3)]$ to study the effect of the alkyl substituents on the transmetallation process (Scheme 1). Since many $^nBu_3SnR$ type compounds are commercially available and they are less toxic than their methyl counterparts, a successful transmetallation to gold would give convenient access to a variety of structurally diverse organogold(I) compounds.

Unfortunately, we found that when using the ^{n}Bu derivative no transmetallation occurs, even under harsh conditions (refluxing toluene for 18 h). Only starting materials and some decomposition (elemental gold) could be observed. The methyl analogue in contrast, readily transfers the phenyl group to gold in refluxing toluene in only 2 h. Based on these results, we focused on trimethyltin derivatives for our subsequent studies.(Scheme 2)

Given our previous success of transferring the 1,8-naphthalenediyl unit to gold(I), we now examined some mononuclear

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* Corresponding author.
E-mail address: fmohr@uni-wuppertal.de (F. Mohr).

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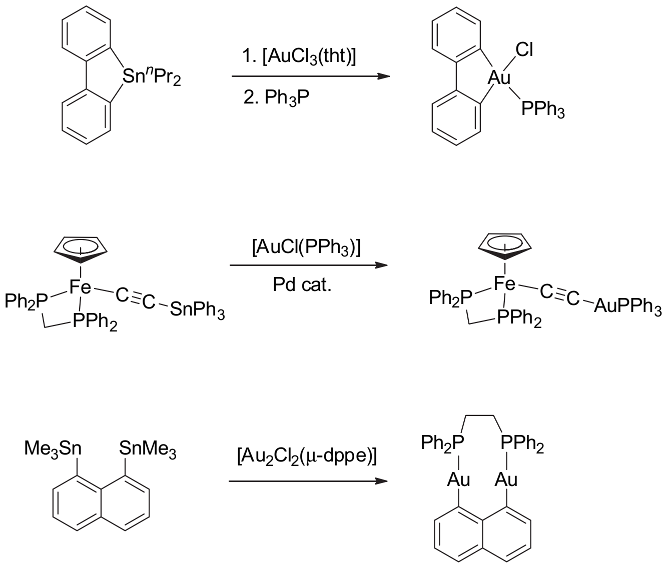
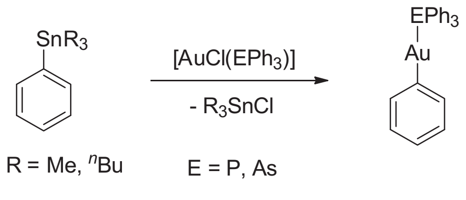


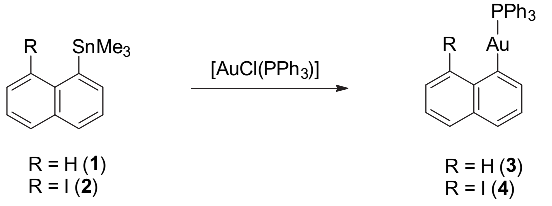
Fig. 1. Examples of organotin species used as transmetallating agents in gold chemistry.

naphthalene derivatives. 1-(Trimethylstannyl)naphthalene (**1**) reacts with [AuCl(PPh$_3$)] in toluene at 70° for 2 h to give the gold(I) naphthyl complex [Au(nap)(PPh$_3$)] (**3**) in 88% yield. The compound was previously prepared using 1-lithionaphthalene in a yield of 68% [22]. Similarly, the 8-iodo derivative (**4**) was also prepared by reacting 1-(trimethylstannyl)-8-iodonaphthalene (**2**) with [AuCl(PPh$_3$)] in hexane at room temperature for 2 h. It is worth noting here, that such a halide-functionalised organogold(I) complex cannot be prepared using organolithium compounds or Grignard reagents. Compounds **2**–**4** were characterised spectroscopically (see Experimental part for details) and also by single crystal X-ray diffraction; the molecular structures are shown in Figs. 2–4.

The organotin compound **2** shows the expected tetrahedral environment about the tin centre, with typical distances and angles for aryl-trimethyl tin compounds. Although the I–Sn separation in **2** of 3.46 Å is less than the sum of the Van der Waals radii (4.15 Å), the Me$_3$Sn unit is bent out of the plane of the naphthyl backbone by *ca.* 0.4 Å, while the iodine atom is bent by *ca.* 0.3 Å in the opposite direction. This deviation from the naphthalene plane of the *peri* substituents is however very small when compared to that of other 1,8-dimetallated naphthalenes [23]. The gold complexes **3** and **4** are structurally very similar; the Au–C and Au–P bond lengths differ only slightly from each other. Similarly, the expected linear angle (174.8°) about the gold centre is practically identical in both compounds. The distance between the gold and iodine atoms in complex **4** [3.1317(7) Å] is less than the sum of the Van der Waals radii (3.64 Å) but longer than a gold-iodine bond (typically around 2.5 Å). This weak attractive interaction between the two *peri* substituents may be responsible for the only very slight buckling of the molecule: the gold atom lies 0.4 Å above the naphthalene plane, whilst the iodine atom is located less than 0.2 Å below this plane.



Scheme 1.



Scheme 2.

In summary, we have shown that Me$_3$SnAr derivatives readily undergo transmetallation with gold(I) species under mild conditions. With this methodology it was possible to prepare a iodo-functionalised naphthylgold(I) compound, which is not accessible by other methods.

3. Experimental

3.1. General

^{1}H, ^{13}C and ^{31}P{^{1}H} NMR spectra were recorded on a 400 MHz Bruker Avance or 600 MHz Bruker Avance III spectrometer. Chemical shifts are quoted relative to external SiMe$_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). Elemental analyses were performed by staff of the microanalytical laboratory of the University of Wuppertal. All reactions were carried out under dinitrogen using standard Schlenk techniques. 1,8-Diiodonaphthalene and 1-(trimethystannyl)naphthalene (**1**) were prepared as described in the literature [24,25]. [AuCl(PPh$_3$)] and [AuCl(AsPh$_3$)] were prepared by reacting [AuCl(tht)] (tht = tetrahydrothiophene) [26] with Ph$_3$P or Ph$_3$As, respectively. All other chemicals and solvents (anhydrous or extra dry grade) were sourced commercially and used as received.

3.2. Transmetallation experiments

Equimolar amounts (*ca.* 0.19 mmol) of the appropriate organotin compound and [AuCl(EPh$_3$)] (E = P, As) were heated in toluene for different periods of time. The volatiles were subsequently removed and the residue examined by NMR spectroscopy. The identity of the formed [AuPh(PPh$_3$)] was confirmed by comparison to literature data [19]. The arsenic derivative was characterised as follows: ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 7.64–7.61$ (m, 2 H, *o*-Ph), 7.50–7.44 (m, 3 H, *m* and *p*-Ph), 7.42–7.37 (m, 15 H, AsPh$_3$). ^{13}C NMR (101 MHz, CDCl$_3$): δ = 141.22 (C-Au), 137.45 (C-As), 133.60 (*o*-AsPh$_3$), 129.18

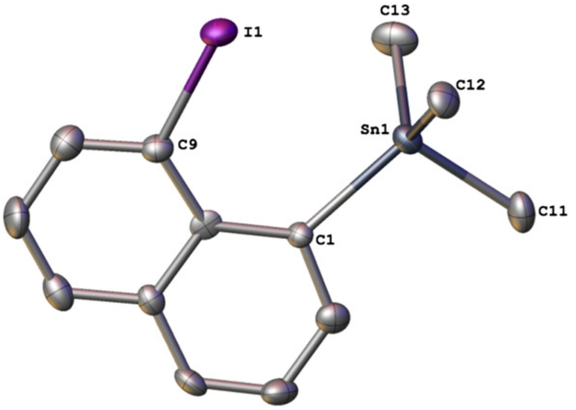


Fig. 2. Molecular structure of 2. Ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity. Selected bond distances [Å]: Sn1-C1 2.182(4), Sn-C11 2.147(5), Sn1-C12 2.135(4), Sn1-C13 2.147(5), I1-C9 2.118(5). Selected angles [°]: C12-Sn1-C13 118.6(2), C12-Sn1-C1 102.94(19), C13-Sn1-C11 102.5(2), C12-Sn1-C1 114.47(17), C13-Sn1-C1 111.76(18), C11-Sn1-C1 104.09(17).