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Transmetalation between Au(I) and Sn(IV) complexes. The reaction mechanism in non-coordinating and coordinating polar solvents

Luciano Canovese [a,*], Carlo Levi [a], Fabiano Visentin [a], Claudio Santo [a], Valerio Bertolasi [b]

[a] *Dipartimento di Scienze Molecolari e Nanosistemi, University Ca' Foscari, Venice, Italy*
[b] *Dipartimento di Chimica and Centro di Strutturistica Diffratometrica, Univesrsity of Ferrara, Ferrara, Italy*

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ABSTRACT

Some novel gold(I) derivatives of the type [LAuCl] (L = DIC, PPh_3, NHCs) have been synthesized and characterized. The products of the transmetalation reaction between these species and tributyl-phenylethynylstannane have been isolated and characterized. An exhaustive kinetic study on the transmetalation reaction has also been carried out in $CHCl_3$ and CH_3CN. The experimental results were discussed in terms of the electronic and steric characteristics of the ligands and an interpretation of the peculiar influence of different solvents on the reaction rates was proposed.

1. Introduction

Recently, the peculiar behavior of gold complexes as homogeneous catalysts was the subject of an exponential growth of publications [1]. However, studies on catalytic reactions in which the key step is traceable back to the transmetalation process involving gold and tin are quite rare. In this respect, the gold catalyzed diyne cyclization involving transfer between diynes and stannyl compounds [2], the allyl–allyl coupling [3], and the alkene carbostannylation [4] represent some remarkable instances. Although the alkynyl derivatives of Au(I) can be prepared in some different methods [5], stoichiometric studies on the transfer reaction of the organic group between organotin reagents and gold(I) derivatives are rare [6] and to the best of our knowledge, no mechanistic investigations on such a reaction are reported in the literature. Owing to the stability to air and moisture and the generally mild reaction conditions that tin derivatives require in the above cited processes, we were prompted to undertake a comprehensive investigation on the influence of the solvent and of the spectator ligands of gold complexes when reacting with stannane derivatives. In particular, we focused our attention on the reactivity and the mechanism when gold(I) substrates of the type [LAuCl] (L = DIC, PPh_3, and NHCs) react with $PhCCSn(nBu)_3$ in $CHCl_3$ and CH_3CN. The studied reaction yields acetylenic derivatives of gold(I) which incidentally have been hypothesized as reaction intermediates in the Sonogashire type cross-coupling reaction involving terminal alkynes and diazonium salts [7]. We have chosen the aforementioned gold(I) complexes since we already had some experience on such ligands and complexes in insertion and oxidative addition reactions [8]. Non polar-non coordinating versus polar-coordinating media were expected to influence the intimate reaction mechanism. Notably, we have carried out the transmetalation reaction without particular care for the environmental conditions. In any case, the reactions went to completion yielding quantitatively the transmetalation products as stable species which were isolated and eventually characterized.

2. Results and discussion

2.1. Synthesis of the complexes [LAuCl]

The complexes [LAuCl] **1A**–**1D** (L = PPh_3, DIC, IMes, IPr) were synthesized according to a published procedure [9] whereas the complexes **1E**–**1H** were synthesized from the corresponding silver carbenic complexes [10] and the precursor [(THT)AuCl] (THT = tetrahydrothiophene) in dichloromethane solution (Scheme 1).

The up-field shift in the ^{13}C NMR spectrum of the $N\underline{C}N$ carbenic carbon signals with respect to the silver precursors ($\Delta\delta \sim 10$ ppm) clearly testified the formation of the gold carbenic derivatives **1E**–**1H**, displaying two well-defined cross peaks with the imidazolic protons in the HMBC spectrum. In the case of **1F** derivative the NMR spectra are coincident with those reported in the literature. [11a]

No remarkable changes in the chemical shifts of all the other signals were observed (Table 1). Notably, the CH_2–Py methylene

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[*] Corresponding author. Tel.: +39 041 2348571; fax: +39 041 2348517.
E-mail address: cano@unive.it (L. Canovese).

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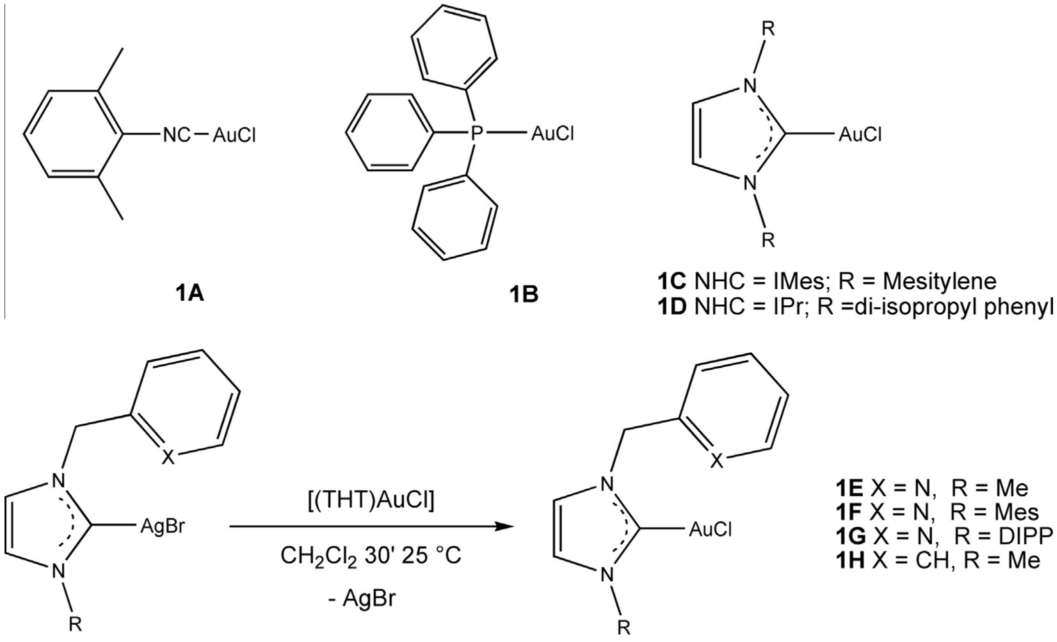

Scheme 1.

Table 1
Selected ^{1}H and ^{13}C signals for the complexes under study.

	C$\underline{H}$	N–C$\underline{H}_2$	H^6_{py}	N–$\underline{C}H_2$	Au–$\underline{C}^{\alpha}\equiv\underline{C}^{\beta}$–Ph	N$\underline{C}$N$_{NHC}$
[(R–NHC–CH$_2$–Py)AgBr] [8]	7/(7.3 ± 0.1)	5.5	8.6	57 ± 0.5	–	181 ÷ 184
[(*i*TBu)AuCl] [11b]		–	–	–	–	168.2
1C	7.09	–	–	–	–	173.4
1D	7.18	–	–	–	–	175.1
1E	6.95/7.19	5.46	8.59	56.4	–	171.6
1F [11b]	6.90/7.38	5.60	8.62	56.5	–	172.3
1G	6.95/7.39	5.62	8.63	56.5	–	173.4
1H	6.89/6.94	5.38	–	55.0	–	171.5
[(*i*TBu)AuCCH] [11b]	7.29	–	–	–	120.0/89.6	187.9
[(IMes)AuCCH] [12]	7.38	–	–	–	124.4/88.0	190.6
2C	7.07	–	–	–	125.9/104.0	189.0
2D [11c]	7.14	–	–	–	125.9/103.7	190.9
2E	6.92/7.14	5.52	8.58	56.1	125.5/105.2	187.7
2F	6.87/7.33	5.68	8.62	56.3	125.5/104.6	188.5
2G	6.91/7.34	5.71	8.63	56.3	125.6/104.5	189.3
2H	6.84/6.90	5.42	–	54.6	125.5/105.2	187.6

groups resonate as a singlet owing to the mono-coordination of R–NHC–CH$_2$–Py and the consequent free rotation of the dangling uncoordinated wing bearing the pyridine fragment.

2.2. Synthesis of the complexes [LAuCCPh]

The synthesis of the alkynyl complexes **2A**–**2H** was easily performed in good yield (75–95%) by adding a slight excess of phenyl–alkynyl–stannane (PhC$\equiv$CSn(*n*Bu)$_3$) to a dichloromethane solution of **1A**–**1H** complexes, according to the reaction reported in Scheme 2.

Under NMR experimental conditions the reactions were complete and measurable in the case of **1B** and **1C** reacting in CDCl$_3$ ($t \sim 30$ min) and in the case of **1D** reacting in CDCl$_3$ and CD$_3$CN ($t \sim 12$ h and 90 min, respectively). In all other cases the reactions are complete but fast in both solvents ($t < 6$ min).

The spectra of **2B** [12] and **2D** [11c] derivatives match the NMR features reported in the literature. Accordingly, the ^{1}H and ^{13}C NMR spectra of the remaining novel complexes are characterized by the appearance of the signals ascribable to the phenyl protons and alkynyl/phenyl carbons of the phenyl–alkynyl moieties. The carbenic carbons N$\underline{C}$N of **2C** and **2E**–**2H** complexes display a marked down-field shift ($\Delta\delta \sim 16$ ppm) with respect to the corresponding silver complexes and in analogy with **2D** [11c] and related derivatives (see Table 1), intense HMBC cross-peaks with the two different imidazolic protons. Moreover, in the phenyl–alkynyl fragment a HMBC cross-peak between the Au–C$\equiv\underline{C}^{\beta}$ carbon and the *o*-phenylic protons is detectable. In any case, no remarkable changes in the chemical shifts of all the other signals were observed when compared with the spectra of complexes **1A**–**1H**.

2.3. Mechanistic investigations: results

Owing to the reduced concentrations, the transmetalation reactions between all the compounds **1A**–**1H** and the phenyl–alkynyl–stannane were slow and easily measurable in CHCl$_3$ by UV–Vis technique, while in CH$_3$CN the only species suitable for spectrophotometric investigation were the complexes **1C**, **1D** and **1G**, the reactions involving the other substrates being too fast.