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

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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 NCN 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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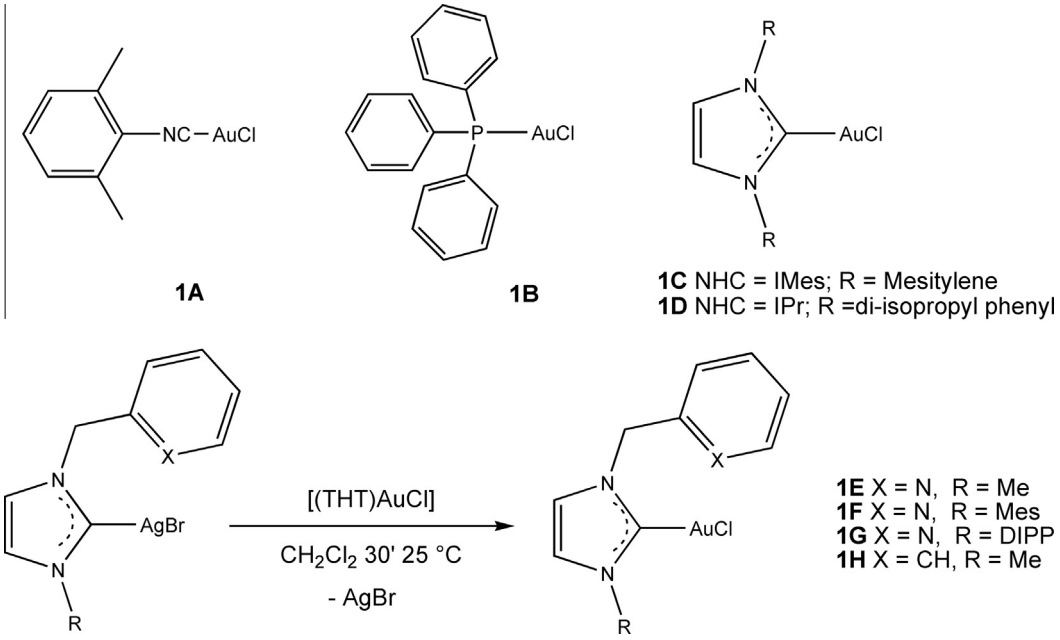


Scheme 1.

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

	C<u>H</u>	N–C<u>H</u>$_2$	H^{6}_{py}	N–<u>C</u>H$_2$	Au–<u>C</u>$^{\alpha}$≡<u>C</u>$^{\beta}$–Ph	N<u>C</u>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]

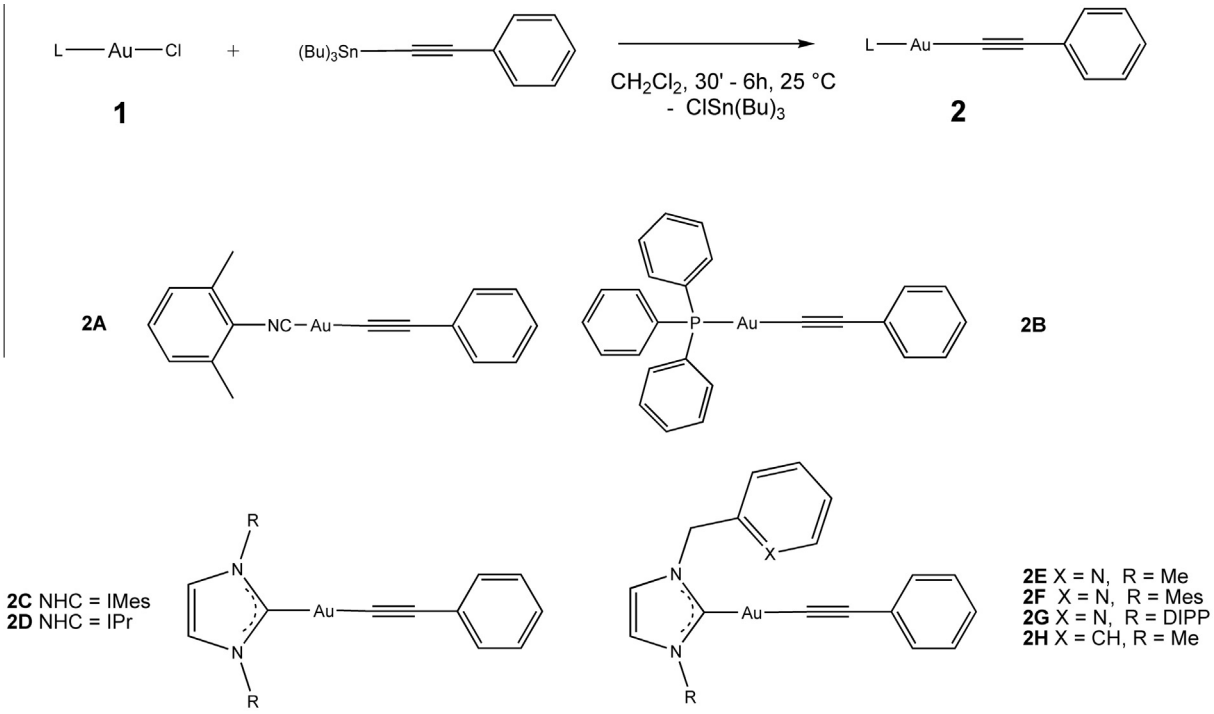
The synthesis of the alkynyl complexes **2A**–**2H** was easily performed in good yield (75–95%) by adding a slight excess of phenyl–alkynyl–stannane (PhC≡CSn(*n*Bu)$_3$) to a dichloromethane solution of **1A**–**1H** complexes, according to the reaction reported in Scheme 2.

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_3CN ($t \sim 12$ 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<u>C</u>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≡<u>C</u>$^{\beta}$ 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_3CN the only species suitable for spectrophotometric investigation were the complexes **1C**, **1D** and **1G**, the reactions involving the other substrates being too fast.



Scheme 2.

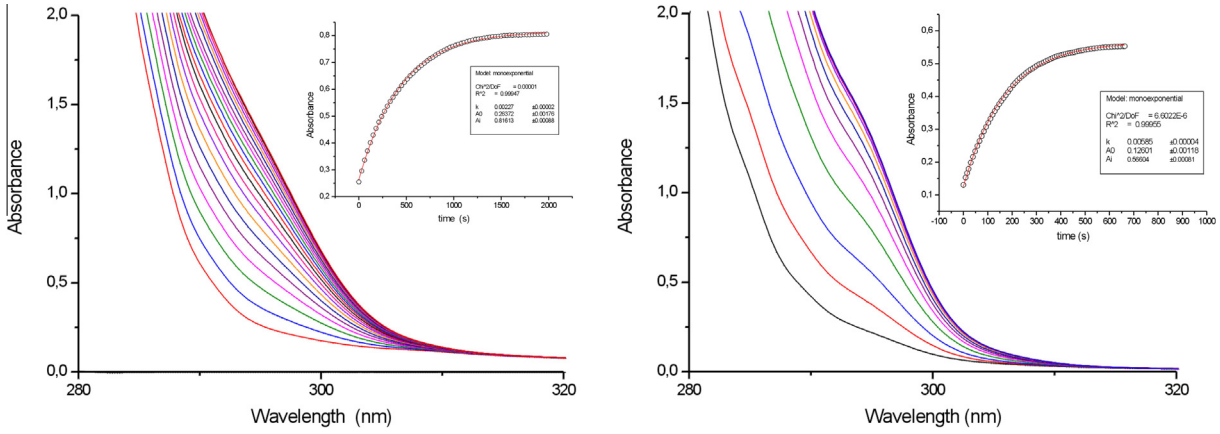


Fig. 1. Absorbance changes (formation of the products) as a function of wavelength and time at 25 °C in $CHCl_3$ (left, $\Delta t = 90$ s) and CH_3CN (Right, $\Delta t = 30$ s) for the reaction **1G** + PhC≡CSn(nBu)$_3$ → **2G** + ClSn(nBu)$_3$. Inset: time dependence of absorbance at $\lambda = 300$ nm ($[\mathbf{1G}]_0 = 1 \times 10^{-4}$ mol dm^{-3}, $[Sn]_0 = 5.5 \times 10^{-3}$ mol dm^{-3}).

In any case the substrates **1** react in the presence of phenyl–alkynyl–stannane under pseudo-first-order conditions ($[Sn]_0 \geqslant 10 \times [Complex]_0$), and the reactions went smoothly to completion. The absorbance change of the reaction mixture with time was analyzed by non-linear regression analysis of the following expression:

$$D_t = (D_0 - D_\infty)e^{-k_{obs}t} + D_\infty \quad (1)$$

where D_0, D_∞ and k_{obs} represent the initial, the final absorbance and the observed rate constant, respectively. (Fig. 1)

2.4. Reaction in $CHCl_3$

In $CHCl_3$ almost all the complexes studied with the exception of the less hindered **1A** display a linear dependence of the calculated k_{obs} on the phenyl–alkynyl–stannane concentrations ($[Sn]_0$) as can be seen in Fig. 2.

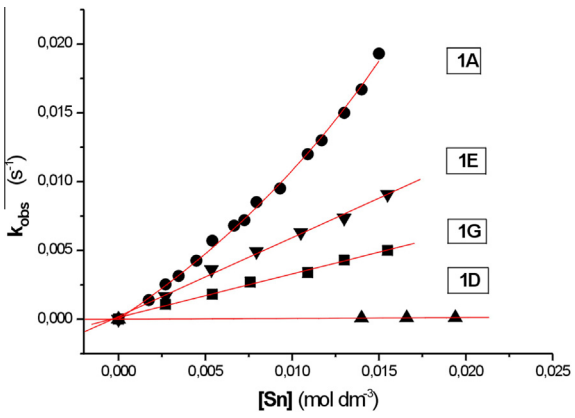
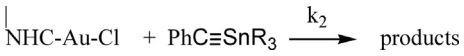


Fig. 2. Polynomial (**1A**) and selected linear (**1D**, **1G**, **1E**) and dependence of k_{obs} vs. $[Sn]_0$ for the transmetalation reaction in $CHCl_3$ at 298 K.



Scheme 3.

We make the hypothesis that the linear dependence of k_{obs} on the stannane concentration is consistent with a simple associative mechanism and hence the reaction progress can be represented by the following Scheme 3.

In such a case the observed rate constant is:

$$k_{obs} = k_2[Sn]_0 \quad (2)$$

Since the reaction depicted in Scheme 3 is governed by an essentially associative path probably involving the concerted formation of a 4-centre cyclic transition state, we were able to undertake a study at various temperatures according to the Eyring approach.

In Fig. 3 the linear regression of $\ln(k_2/T)$ versus $1/T$ in the case of complex **1G** is reported. From linear regression of the Eyring equation we obtained $\Delta H^* = 34 \pm 3$ kJ mol^{-1} and $\Delta S^* = -142 \pm 10$ J mol^{-1} K^{-1}, respectively.

The quite large negative value of the activation entropy and the influence of the steric hindrance of the involved complexes on the rate constants (*vide infra*) strongly support the hypothesis of a four –centre associative mechanism [13]. Incidentally, a similar value of ΔS^* was measured in the case of the transmetalation reaction between aryl complexes of Pd(II) and the same alkynyl stannane used in this study in $CHCl_3$ and CH_3CN ($\Delta S^* = -139$ and -146 J mol^{-1} K^{-1}, respectively) [14].

Accordingly, the k_2 values determined in the case of the complexes **1A**–**1D** are remarkably influenced by the buried volume of the spectator ligands. Thus, the complex **1D** bearing the most encumbered IPr ligand (%W = 29) reacts slower than the homologue **1C** (%W = 26). The comparable higher reaction rates measured for the homologue series **1E**–**1H** are probably due to the reduced steric requirements of the ancillary ligand. Consistently, within this series the less encumbered methyl substituted **1H** and **1E** display an enhanced reactivity with respect to the mesityl and di-isopropyl phenyl substituted **1G** and **1F**.

Remarkably, despite the reduced buried volume (%W = 21) complex **1B** displays the same reactivity as **1C** owing to the different electronic influence that the π-acid phosphine exerts on the metal centre with respect to that of the almost pure σ-donor carbene. Apparently, the increase of electronic density on the metal centre induced by the NHC ligand enhances the scarce tendency of gold(I) to π-back donation. [see Ref. [1m] and Refs. therein]

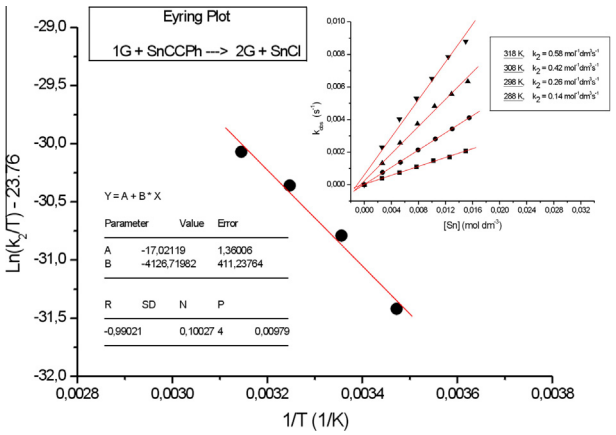


Fig. 3. Eyring plot for the reaction **1G** + RSnCCPh → **2G** + RSnCl (top insert: linear plots of k_{obs} vs. [RSnCCPh] at different temperatures).

Table 2
Kinetic and equilibrium constants.

Complex	$CHCl_3$	CH_3CN	
	k_2 (mol^{-1}dm^{3}s^{-1})	k_1 (s^{-1})	K_i
1A	0.76 ± 0.08		
1B	0.07 ± 0.01		
1C	0.07 ± 0.01	$(6.7 \pm 0.5) \times 10^{-3}$	129 ± 11
1D	0.0058 ± 0.0003	$(1.2 \pm 0.3) \times 10^{-3}$	322 ± 90
1E	0.57 ± 0.02		
1F	0.31 ± 0.01		
1G	0.26 ± 0.01	$(1.4 \pm 0.1) \times 10^{-2}$	128 ± 13
1H	0.52 ± 0.02		

Reasonably, formation of the π-adduct between the metal and the alkynic electronic system of the incoming stannane [15] probably represents the first step of the overall transmetalation process. Therefore, the enhanced electronic density induced by the ligand IMes on the gold centre makes this stage energetically more accessible and consequently favours the reaction progress.

We do not have at the moment an unequivocal explanation for the behaviour of complex **1A** for which the rate equation is described by the function:

$$k_{obs} = \alpha[Sn]_0 + \beta[Sn]_0^2 \quad (3)$$

We surmise that the phenyl–alkynyl–stannane will rapidly but partially coordinate to the fairly unhindered DIC isocyanide. The ensuing equilibrium mixture will react with the free phenyl–alkynyl–stannane present in excess to give the reaction products. In that case the observed rate constant would be:

$$k_{obs} = \frac{k_2[Sn]_0 + k_2 * K[Sn]_0^2}{1 + K[Sn]_0} \quad (4)$$

which is virtually undistinguishable from (3 when $\alpha = k_2$ and $\beta = k_2{}^*K$ and the value of the equilibrium constant K is small.[1] Under this hypothesis we can compare the linear part of Eq. (3) to the other measured rate constants and not surprisingly the less steric demanding complex **1A** displays the highest reactivity (see Table 2).

2.5. Reaction in CH_3CN

The dependence of the observed rate constants of complexes **1** on stannane concentration in CH_3CN in the measurable cases of complexes **1C**, **1D**, and **1G** is reported in Fig. 4:

The dependence of k_{obs} on $[Sn]_0$ in Fig. 4 can be described by the equation:

$$k_{obs} = \frac{\theta[Sn]_0}{\delta + \gamma[Sn]_0} \quad (5)$$

2.6. The proposed mechanism

Although the nature of the solvent can heavily influence the reaction rate thanks to its interaction with the transition state or the intermediate involved in the reaction, it is quite unusual to observe a change or an apparent change in the mechanism as in the

[1] No reaction was observed when free DIC isocyanide was added to a solution of alkynyl stannane in $CDCl_3$. However, we cannot exclude that the stannane attacks the unhindered isocyanide activated by coordination to a metal centre. No changes in the NMR spectra are experimentally observed upon stannane addition to the gold complex. This is probably due to the fact that the extent of pre-coordination of the stannane on the activated DIC, if any, is small. A similar dependence of the rate constant on the nucleophile concentration was observed in the case of attack of amines to carbene–isocyanide derivatives of gold(I) in $CHCl_3$ (Ref. [7a]) although in that case the equilibrium constant was not negligible.

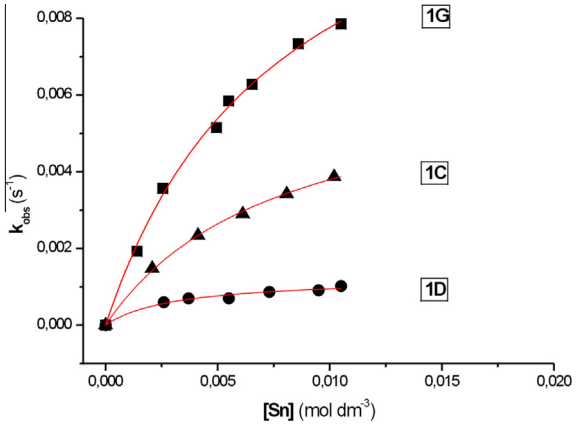


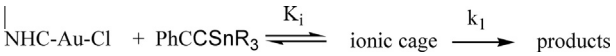
Fig. 4. Non-linear dependence of k_{obs} vs. $[Sn]_0$ for the transmetalation reaction in CH_3CN at 298 K.

present case. Therefore, an attempt at interpreting the observed kinetic laws is in order.

The most obvious interpretation could be traced back to the pre-equilibrium formation of a gold(I) solvated species which rapidly adds the alkynyl stannane or, alternatively, to the formation of a π-adduct bearing the stannane coordinated. Such a compound might be a di-nuclear gold(I) species bearing one bridged alkyne coordinated *via* σ to one gold atom and π to the other [15]. Eventually, the π-adduct intermediate should rearrange slowly to the reaction products. These hypotheses, however, are in disagreement with the fact that no hints of dissociation of the complexes of type **1** are observed by conductivity measurements in CH_3CN. Moreover, dechlorination by AgOTf of type **1** complexes yields the solvato species $[(L)Au(CH_3CN)]^+$ which immediately forms the gold(I) alkynyl derivative upon addition of the alkynyl–stannane. Although the chloride ion is not present in solution, at variance with the reaction rates measured under NMR or UV–Vis conditions, the latter experimental fact seems to suggest that the transmetallation process would proceed fast when gold(I) solvato complexes are present in solution.

The hypothetical formation of a π-adduct bearing the stannane coordinated was also ruled out since no traces of species in equilibrium with the reagents (at concentrations of the reagents $\sim 1 \times 10^{-2}$ mol dm^{-3}) can be detected by NMR investigation although the values of the equilibrium constant measured in the kinetic studies (*vide infra*) are such that at least about 40% of the reagents should be converted into the equilibrium mixture.

In our opinion, a plausible explanation should take into account that acetonitrile has a dielectric constant and a dipole momentum ($\varepsilon_r = 37$; $\mu = 3.9$ D) remarkably higher than those of $CHCl_3$ ($\varepsilon_r = 4.8$; $\mu = 1.0$ D) in addition to its appreciable coordination capability as witnessed by the gold(I) acetonitrile complexes [16]. Moreover, type **1** complexes are characterized by a well defined dipole moments which were calculated to be 9.1 and 0.9 D, in the case of the complex **1D** and of the phenyl–alkynyl–stannane respectively [17]. Under these experimental conditions, a diffusion controlled formation of an ionic cage constituted by the gold complex **1** surrounded by solvating acetonitrile molecules and the solvated phenyl–alkynyl–stannane is likely. The subsequent step could be represented by the slow formation of an active intermediate. This step should be controlled by the rotational motion of the molecules and clearly depends on the mutual steric requirements of the particles in the cage. Eventually, when the particles reach the correct orientation, the intermediate will rapidly collapse into the reaction products. The overall mechanism of the diffusion controlled reaction [18] is described in Scheme 4 in which the expression ionic



Scheme 4.

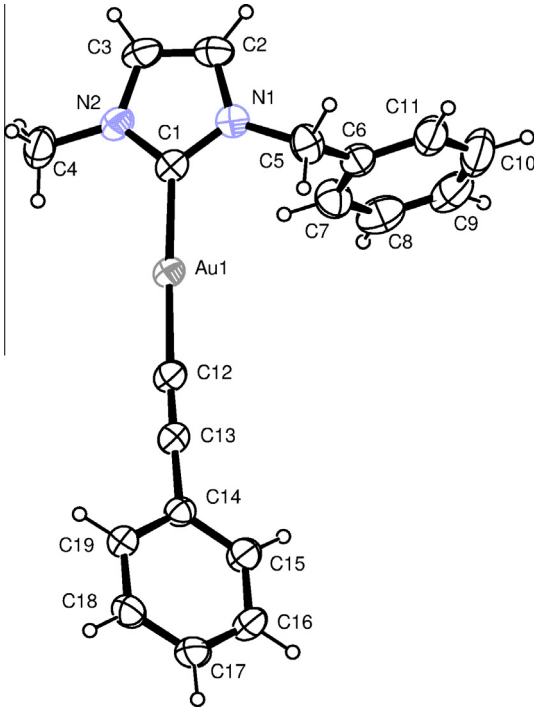


Fig. 5. ORTEP view of compound **2H** showing the thermal ellipsoids at 30% probability level.

cage represents the gold complex **1** surrounded by solvating acetonitrile molecules interacting with the solvated phenyl–alkynyl–stannane:

The observed reaction rate would obey the equation:

$$k_{obs} = \frac{k_1 K_i [Sn]_0}{1 + K_i [Sn]_0} \quad (6)$$

Eq. (6) is coincident with Eq. (5) with $k_1 K_i = \theta$, $1 = \delta$ and $K_i = \gamma . k_1$ represents the rate determining step involving the concerted formation of the 4-centre cyclic transition state, whereas K_i is strictly related to the fast formation of the ionic cage which is not observable by NMR experiment. Consistently, as already stated, no particular changes in the spectrum of the reaction mixture were noticed when the stannane was added to the complex in NMR experiments. As can be seen in Table 2 the K_i values are virtually independent of the nature of the complexes[2] whereas k_1 is strongly influenced by the steric hindrance of the gold derivatives.

2.7. Crystal structure determination

ORTEP [19] view of the complex of **2H** is shown in Fig. 5. A selection of bond distances and angles is given in Table 3.

The compound **2H** is a gold(I) complex containing both a carbene and an alkynyl ligand. The Au atom is in an essentially linear

[2] In the case of complexes **1C** and **1G** the shape of the curve allows an accurate determination of the K_i constants and the ensuing values are indistinguishable (Table 2). Conversely, the K_i value for complex **1D** is poorly determined and affected by a large error owing to the slight curvature of the corresponding plot (Fig. 4). Therefore, in our opinion this value should not be far from those of the other complexes since it reflects the extent of an ionic aggregation that is mostly controlled by the dipole moment of the species involved.

Table 3
Selected bond distances and angles (Å and degrees) for **2H**.

Distances			
Au1–C1	2.018(4)	Au1–C12	1.982(4)
C1–N1	1.352(5)	C1–N2	1.345(5)
C2–N1	1.384(6)	C3–N2	1.377(6)
C12–C13	1.199(6)	C13–C14	1.444(6)
Angles			
C1–Au1–C12	177.8(2)	Au1–C12–C13	176.8(4)
C12–C13–C14	177.6(5)	Au1–C1–N1	126.2(3)
Au1–C1–N2	129.6(3)	N1–C1–N2	104.2(3)
C1–N1–C2	110.4(4)	C1–N2–C3	111.3(4)

coordination with a $C1_{carbene}$–Au–$C12_{alkynyl}$ angle of 177.8(2)°. The slight difference between Au–C1 and Au–C12 bond distances of 2.018(4) and 1.982(4) Å, respectively, can be accounted for the different hybridization of C1(sp^2) and C12(sp) atoms. These distances are similar to those observed in other alkynyl–carbene–gold(I) complexes [20–24]. The carbon–carbon bond length of 1.199(6) Å between C12 and C13 corresponds to a typical C≡C triple bond in this class of complexes. The carbene C1–N1 and C1–N2 bond distances of 1.352(4) and 1.345(5) Å, respectively, are intermediate between those corresponding to simple and double C–N bonds, suggesting that there is a significant electron delocalization in the N–C–N moiety. No Au···Au short interactions were observed in the crystal packing.

3. Conclusion

We have synthesized several Au(I) complexes of the type [LAuCl] (L = NHC, Phosphine, Isocyanide) and we have studied their reactivity toward the transmetalation with phenyl alkynyl stannane in $CHCl_3$ and in CH_3CN to give the derivatives [LAuCCPh]. The reaction rates and the mechanism are strongly influenced by the solvent. On the basis of an exhaustive kinetic study we were able to propose an interpretation of the experimental data and a plausible mechanism. The solid state structure of complex **2H** was resolved.

4. Experimental

4.1. Solvents and reagents

CH_2Cl_2 and CH_3CN were distilled over CaH_2 under inert atmosphere (Ar), $CHCl_3$ was distilled and stored over silver foil. All the other chemicals were commercially available grade products unless otherwise stated. The complexes [(R–NHC–CH_2–Py)AgBr] [9] (R = Me, Mes, DIPP), [(Me–NHC–CH_2–Ph)AgBr] [10a] and [(L)AuCl] (L = PPh_3, DIC, IMes, IPr, Mes–NHC–CH_2–Py) were prepared following literature procedures. [9,11b]

4.2. IR, NMR and UV–Vis measurements

The IR, ^1H, $^{13}C\{^1H\}$ and ^{31}P NMR spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer and on a Bruker 300 Avance spectrometer. The proton and carbon assignment was performed by ^1H–^1H COSY, ^1H–^{13}C HMBC and ^1H–^{13}C HMQC experiments. UV–Vis spectra were taken on a Perkin–Elmer Lambda 40 spectrophotometer equipped with a Perkin–Elmer PTP6 (Peltier Temperature Program) apparatus.

4.3. Preliminary studies and kinetic measurements

All the transmetalation reactions were preliminarily analyzed by ^1H NMR technique by dissolving the complex under study [(L)AuCl] (L = PPh_3, DIC, IMes, IPr, R–NHC–CH_2–Py, Me–NHC–CH_2–Ph) in 0.6 ml of $CDCl_3$ or CD_3CN ($[complex]_0 \approx 0.02$ mol dm^{-3}) at 298 K. An appropriate aliquot of pure phenyl-alkynyl-stannane [PhCCSn(nBu)$_3$] was added ($[Sn]_0 \approx 0.02$ mol dm^{-3}) and the reaction was followed to completion by monitoring the disappearance of the signals of the starting complex and the concomitant appearance of those of the phenyl–alkynyl–gold complex.

A UV–Vis preliminary investigation was also carried out with the aim of determining the best wavelength for spectrophotometric analysis, corresponding to the widest change in absorbance. To this purpose, the complex under study dissolved in 3 ml of freshly distilled $CHCl_3$ ($[complex]_0 \approx 1 \times 10^{-4}$ mol dm^{-3}) was placed in the thermostatted cell compartment (298 K) of the UV–Vis spectrophotometer and aliquots of concentrated solution of phenyl–alkynyl–stannane ($[Sn] \approx 0.25$ mol dm^{-3}) were added. Due to the reduced solubility of the phenyl–alkynyl–stannane in CH_3CN, a concentrated solution of the latter ($[Sn]_0 = 0.25$ mol dm^{-3}) cannot be prepared. Therefore, the preliminary investigation was carried out by adding to the phenyl–alkynyl–stannane dissolved in 3 ml of prethermostatted anhydrous CH_3CN ($[Sn]_0 \approx 1 \times 10^{-3}$ - mol dm^{-3}), aliquots of concentrated solution of the complex under study ($[complex]_0 \approx 0.1$ mol dm^{-3}). The absorbance change was monitored in the 280–320 nm wavelength range. The kinetics of transmetalation were recorded at $\lambda = 300$ nm ($[Sn]_0$ 1×10^{-3} - $\div 2 \times 10^{-2}$ mol dm^{-3}in $CHCl_3$ and $1 \times 10^{-3} \div 1 \times 10^{-2}$ mol dm^{-3} in CH_3CN) by adding aliquots of the mother solution of phenyl–alkynyl–stannane ($[Sn]_0 \approx 0.25$ mol dm^{-3}) to a solution of the complex under study in 3 ml of freshly distilled $CHCl_3$ ($[complex]_0 \approx 1 \times 10^{-4}$ mol dm^{-3}) or by adding aliquots of the mother solution of the complex under study to solutions of stannane in 3 ml of anhydrous CH_3CN ($[complex]_0 \approx 1 \times 10^{-4}$ mol dm^{-3}, $[Sn]_0 = 1 \times 10^{-3} \div 1 \times 10^{-2}$ mol dm^{-3}) respectively.

4.4. Synthesis of the [(NHC)AuCl] complexes

4.4.1. [(Me–NHC–CH_2–Py)AuCl] (**1E**)

To a stirred solution of [(Me–NHC–CH_2–Py)AgBr] (0.451 g, 1.25 mmol) in 10 ml of dichloromethane, [(THT)AuCl] was added (0.328 g, 1.2 mmol). The reaction proceeds at room temperature with the concomitant precipitation of AgBr. After 2 h the reaction mixture was treated with activated charcoal and filtered through a Celite filter. The resulting clear solution, concentrated under reduced pressure, yielded the crude product upon addition of diethyl ether. The white residue was filtered off and washed with diethyl ether (3 × 3 ml) and n-pentane (3 × 3 ml). The resulting solid was dried under vacuum.

Yield: 73%, white solid. ^1H NMR ($CDCl_3$, $T = 298$ K, ppm): δ 3.86 (s, 3 H, NCH_3), 5.46 (s, 2 H, NCH_2), 6.95 (d, 1 H, HC=CH im, $J = 1.8$ Hz), 7.19 (d, 1 H, CH=CH im, $J = 1.8$ Hz), 7.28 (t, 1 H, 5-pyr, $J = 6.2$ Hz), 7.47 (d, 1 H, 3-Pyr, $J = 7.6$ Hz), 7.72 (td, 1 H, 4-Pyr, $J = 7.6$, 1.6 Hz), 8.59 (d, 1 H, 6-Pyr, $J = 4.8$ Hz). ^{13}C NMR $\{^1H\}$ ($CDCl_3$, $T = 298$ K, ppm): δ 38.2 ($N\underline{C}H_3$), 56.4 ($N\underline{C}H_2$), 121.3 ($H\underline{C}$=CH im), 121.8 (HC=$\underline{C}$H im), 122.9 (C3-pyr), 123.4 (C5-pyr), 138.0 (C4-pyr), 149.7 (C6–pyr), 154.6 (C2-pyr), 171.6 ($N\underline{C}N$). IR (KBr pellet, cm^{-1}): $\nu = 2925$ (CH), 1592(CN), 1469 (CC). *Anal.* Calc. For $C_{10}H_{11}AuClN_3$: C, 29.61; H, 2.73; N, 10.36. Found: C, 29.47; H, 2.61; N, 10.22%.

The following complexes were prepared under similar conditions by using the appropriate [(NHC)AgBr] precursor.

4.4.2. [(Mes–NHC–CH_2–Py)AuCl] (**1F**)

Yield: 89%, white solid.

^1H NMR ($CDCl_3$, $T = 298$ K, ppm): δ 2.02 (s, 6 H, o-mesityl CH_3), 2.34 (s, 3 H, p-mesityl CH_3), 5.6 (s, 2 H, NCH_2), 6.9 (d, 1 H, HC=CH im, $J = 1.8$ Hz), 6.97 (s, 2 H, m-mesityl H), 7.31 (m, 1 H, 5-pyr), 7.38 (d, 1 H, HC=CH im, $J = 2.1$ Hz), 7.5 (d, 1 H, 3-pyr, $J = 7.8$ Hz), 7.75

(td, 1 H, 4-pyr, J = 9.0, 1.8 Hz), 8.62 (d, 1 H, 6-pyr, J = 4.8 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 17.8 (o-mesityl $\underline{C}H_3$), 21.1 (p-mesityl $\underline{C}H_3$), 56.5 ($N\underline{C}H_2$), 121.4 ($H\underline{C}$=CH im), 122.5 (C3-pyr), 123.5 (HC=$\underline{C}$H im), 129.1 (C5-pyr), 129.4 (m-mesityl $\underline{C}$H), 134.7 (C_{quat} mesityl), 137.5 (C4-pyr), 139.7 (C_{quat} mesityl), 149.8 (C6-pyr), 154.8 (C2-pyr), 172.3 ($N\underline{C}N$). IR (KBr pellet, cm^{-1}): ν = 2962(CH), 1593(CN), 1468(CC). *Anal.* Calc. for $C_{18}H_{19}AuClN_3$: C, 42.41; H, 3.76; N, 8.24. Found: C, 42.27; H, 3.49; N, 8.15%.

4.4.3. [(DIPP–NHC–CH_2–Py)AuCl] (**1G**)

Yield: 63%, white solid.

^1H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.12 (d, 6 H, *i*Pr–CH_3, J = 6.9 Hz), 1.29 (d, 6 H, *i*Pr–CH_3, J = 6.9 Hz), 2.4 (septet, 2 H, *i*Pr–CH), 5.62 (s, 2 H, NCH_2), 6.95 (d, 1 H, HC=CH im, J = 1.8 Hz), 7.27 (d, 2 H, m-aryl H, J = 15.6 Hz), 7.32 (dd, 1 H, 5-pyr, J = 4.8, 7.5 Hz), 7.39 (d, 1 H, HC=CH im, J = 1.8 Hz), 7.46–7.52 (m, 2 H, p-aryl H, 3-pyr), 7.76 (td, 1 H, 4-pyr, J = 7.5, 1.8 Hz), 8.63 (d, 1 H, 6-pyr, J = 4.5 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 24.2, 24.3 (*i*Pr–CH_3), 28.3 (*i*Pr-CH), 56.5 ($N\underline{C}H_2$), 121.0 ($H\underline{C}$=CH im), 122.6 (C3-pyr), 123.5 (C5-pyr), 123.6 (HC=$\underline{C}$H im), 124.1 (m-aryl $\underline{C}$H), 130.5 (p-aryl $\underline{C}$H), 134.0 (C_{quat} aryl), 137.4 (C4-pyr), 145.6 (o-aryl $\underline{C}$), 149.6 (C6–pyr), 154.7 (C2-pyr), 173.4 ($N\underline{C}N$). IR (KBr pellet, cm^{-1}): ν = 2963 (CH), 1592(CN), 1469(CC). *Anal.* Calc. for $C_{21}H_{25}AuClN_3$: C, 45.70; H, 4.57; N, 7.61. Found: C, 45.42; H, 4.35; N, 7.48%.

4.4.4. [(Me–NHC–CH_2–Ph)AuCl] (**1H**)

Yield: 91%, white solid.

^1H NMR ($CDCl_3$, T = 298 K, ppm): δ 3.87 (s, 3 H, NCH_3), 5.38 (s, 2 H, NCH_2), 6.89 (d, 1 H, HC=CH im, J = 1.8 Hz), 6.94 (d, 1 H, CH=CH im, J = 1.8), 7.32–7.42 (m, 5 H, benzyl H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 38.2 ($N\underline{C}H_3$), 54.9 ($N\underline{C}H_2$), 120.3 ($H\underline{C}$=CH im), 122.2 (HC=$\underline{C}$H im),127.9, 128.7, 129. 0, 134.9 (benzyl C), 171.5 ($N\underline{C}N$). IR (KBr pellet, cm^{-1}): ν = 2942(CH), 1566 (CN), 1451(CC). *Anal.* Calc. for $C_{11}H_{12}AuClN_2$: C, 32.65; H, 2.99; N, 6.92. Found: C, 32.51; H, 2.87; N, 6.79%.

4.5. Synthesis of the [(L)AuC≡CPh] complexes

4.5.1. [(DIC)AuC≡CPh] (**2A**)

To a stirred solution of [(DIC)AuCl] (0.1 g, 0.28 mmol) in 10 ml of dichloromethane, pure [PhCCSn(*n*Bu)$_3$] was added (0.152 ml, 0.41 mmol). After 2 h the reaction mixture was treated with activated charcoal and filtered through a Celite filter. The resulting clear solution, concentrated under reduced pressure, yielded the crude product upon addition of pentane. The white residue was filtered off and washed with diethyl ether (3 × 3 ml) and n-pentane (3 × 3 ml). The resulting solid was dried under vacuum.

Yield: 91%, white solid. ^1H NMR ($CDCl_3$, T = 298 K, ppm): δ 2.46 (s, 6 H, o-aryl CH_3), 7.19 (d, 2 H, m-aryl H, J = 7.2 Hz), 7.22–7.30 (m, 3 H, m/p-phenyl H), 7.35 (t, 1 H, p-aryl H, J = 8.1 Hz), 7.49–7.52 (m, 2 H, o-phenyl H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 18.6 (o-aryl $\underline{C}H_3$), 103.9 (Au$\underline{C}$CPh), 124.5 (Au$\underline{C}$CPh), 126.9, 128.3 (m/p-phenyl $\underline{C}$H), 127.8 (m-aryl $\underline{C}$H), 130.8 (p-aryl $\underline{C}$H), 132.4 (o-phenyl $\underline{C}$H), 136.1 ($N\underline{C}N$). IR (KBr pellet, cm^{-1}): ν = 2958, 2914(CH), 2208(CN), 1466, 1382(CC). *Anal.* Calc. for $C_{17}H_{14}AuN$: C, 47,57; H, 3,29; N, 3,26. Found: C, 47,44; H, 3,18; N, 3,20%.

The following complexes were prepared under similar conditions by using the appropriate [(NHC)AuCl] precursor.

4.5.2. [(IMes)AuC≡CPh] (**2C**)

Yield: 95%, white solid. ^1H NMR ($CDCl_3$, T = 298 K, ppm): δ 2.14 (s, 12 H, mesityl CH_3), 2.36 (s, 6 H, mesityl CH_3), 7.01 (s, 4 H, m-mesityl H), 7.07 (s, 2 H, HC=CH im), 7.08–7.17(m, 3 H, phenyl H) 7.34–7.37 (m, 2H, phenyl H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 17.8 (o-mesityl $\underline{C}H_3$), 21.1 (p-mesityl $\underline{C}H_3$), 104.0 (Au$\underline{C}$CPh), 122.1 (HC=CH im), 125.5 (C_{quat} phenyl), 125.9 (Au$\underline{C}$CPh), 127.5 (m/p-phenyl $\underline{C}$H), 129.4 (m-mesityl $\underline{C}$H), 132.2 (o-phenyl $\underline{C}$H), 134.8 (C_{quat} mesityl), 139.4 (C_{quat} mesityl), 189.0 ($N\underline{C}N$). IR (KBr pellet, cm^{-1}): ν = 2915, 2857(CH), 2113, 1487(CC), 1608(CN). *Anal.* Calc. for $C_{29}H_{29}AuN_2$: C, 57.81; H, 4.85; N, 4.65. Found: C, 57.69; H, 4.74; N, 4.51%.

4.5.3. [(Me–NHC–CH_2–Py)AuCCPh] (**2E**)

Yield: 75%, white solid. ^1H NMR ($CDCl_3$, T = 298 K, ppm): δ 3.89 (s, 3 H, NCH_3), 5.51 (s, 2 H, NCH_2), 6.92 (d, 1 H, HC=CH im, J = 1.5 Hz), 7.14 (d, 1 H, CH=CH im, J = 1.5 Hz), 7.18–7.28 (m, 4 H, 5-pyr, m/p-phenyl H), 7.47 (d, 1 H, 3-pyr, J = 7.6 Hz), 7.52 (m, 2 H, o-phenyl H), 7.71 (td, 1 H, 4-pyr, J = 7.8, 1.5 Hz), 8.58 (d, 1 H, 6-pyr, J = 3.9 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 37.9 ($N\underline{C}H_3$), 56.1 ($N\underline{C}H_2$), 105.2 (Au$\underline{C}$CPh), 121.0 ($H\underline{C}$=CH im), 122.0 (HC=$\underline{C}$H im), 122.8 (C3-pyr), 123.3 (C5–pyr), 125.5 (Au$\underline{C}$CPh), 126.2 (p-phenyl $\underline{C}$H), 127.7 (m-phenyl $\underline{C}$H), 127.9 (C_{quat} phenyl), 132.2(o-phenyl $\underline{C}$H), 137.2 (C4-pyr), 149.5 (C6-pyr), 155.0 (C2-pyr), 187.7 ($N\underline{C}N$). IR (KBr pellet, cm^{-1}): ν = 2925(CH), 2113, 1469(CC), 1592(CN). *Anal.* Calc. for $C_{18}H_{16}AuN_3$: C, 45.87; H, 3.42; N, 8.92. Found: C, 45.76; H, 3.37; N, 8.80%.

4.5.4. [(Mes–NHC–CH_2–Py)AuC≡CPh] (**2F**)

Yield: 75%, white solid. ^1H NMR ($CDCl_3$, T = 298 K, ppm): δ 2.05 (s, 6 H, o-mesityl CH_3), 2.35 (s, 3 H, p-mesityl CH_3), 5.7 (s, 2 H, NCH_2), 6.87 (d, 1 H, HC=CH im, J = 2.1 Hz), 6.97 (s, 2 H, m-mesityl H), 7.18 (m, 3 H, m/p-phenyl H), 7.3 (m, 1 H, 5-pyr), 7.33 (d, 1 H, HC = CH im, J = 2.1 Hz), 7.42 (d, 1 H, o-phenyl H, J = 1.5 Hz), 7.5 (d, 1 H, o-phenyl H, J = 1.5 Hz), 7.51 (d, 1 H, 3-pyr, J = 7.8 Hz), 7.74 (td, 1 H, 4-pyr, J = 7.5, 1.8 Hz), 8.63 (d, 1 H, 6–pyr, J = 3.3 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 17.8 (o-mesityl $\underline{C}H_3$), 21.0 (p-mesityl $\underline{C}H_3$), 56.3 ($N\underline{C}H_2$), 104.6 (Au$\underline{C}$CPh), 121.0 ($H\underline{C}$=CH im), 122.5 (HC=$\underline{C}$H im), 122.6 (C3-pyr), 123.3 (C5-pyr), 125.5 (Au$\underline{C}$CPh), 126.1 (p-phenyl $\underline{C}$H), 127.6 (m-phenyl $\underline{C}$H), 129.3 (m-mesityl $\underline{C}$H), 132.2 (o-phenyl $\underline{C}$H), 134.7 (C_{quat} mesityl), 137.3 (C4–pyr),139.3 (C_{quat} mesityl), 149.5 (C6–pyr), 155.3 (C2-pyr), 188.5 ($N\underline{C}N$). IR (KBr pellet, cm^{-1}): ν = 2962(CH), 2113, 1468(CC), 1593(CN). *Anal.* Calc. for $C_{26}H_{24}AuN_3$: C, 54.27; H, 4.20; N, 7.30. Found: C, 54.15; H, 4.13; N, 7.21%.

4.5.5. [(DIPP–NHC–CH_2-Py)AuC≡CPh] (**2G**)

Yield: 93%, white solid. ^1H NMR ($CDCl_3$, T = 298 K, ppm): δ 1.12 (d, 6 H, *i*Pr–CH_3, J = 6.9 Hz), 1.33 (d, 6 H, *i*Pr–CH_3, J = 6.9 Hz), 2.4 (septet, 2 H, *i*Pr–CH), 5.71 (s, 2 H, NCH_2), 6.91 (d, 1 H, HC=CH im, J = 1.8 Hz), 7.1–7.21 (m, 3 H, m/p-phenyl H), 7.26 (d, 2 H, m-aryl H), 7.31 (m, 1 H, 5-pyr) 7.34 (d, 1 H, HC=CH im, J = 1.8), 7.43 (m, 2 H, o-phenyl H), 7.47 (t, 1 H, p-aryl H, J = 7.8 Hz), 7.53 (d, 1 H, 3-pyr, J = 7.8 Hz,), 7.75 (td, 1 H, 4-pyr, J = 7.5, 1.8 Hz), 8.63 (d, 1 H, 6-pyr, J = 4.7 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 24.2, 24.5 (*i*Pr–$\underline{C}H_3$), 28.4 (*i*Pr–$\underline{C}$H), 56.3 ($N\underline{C}H_2$), 104.5 (Au$\underline{C}$CPh), 120.8 ($H\underline{C}$=CH im), 122.6 (C3–pyr), 123.3 (C5-pyr), 123.8 (HC = $\underline{C}$H im), 124.0 (m-aryl $\underline{C}$H), 125.6 (Au$\underline{C}$CPh), 126.0 (p-phenyl $\underline{C}$H), 127.6 (m-phenyl $\underline{C}$H), 128.3 (Cquat phenyl), 130.3 (p-aryl $\underline{C}$H), 132.2 (o-phenyl $\underline{C}$H), 134.2 (C_{quat} aryl), 137.3 (C4-pyr), 145.7 (o-aryl C), 149.5 (C6-pyr), 155.2 (C2–pyr), 189.3 ($N\underline{C}N$). IR (KBr pellet, cm^{-1}): ν = 2963(CH), 2113, 1469(CC), 1592(CN). *Anal.* Calc. for $C_{29}H_{30}AuN_3$: C, 56.40; H, 4.90; N, 6.80. Found: C, 56.29 H, 4.79; N, 6.67%.

4.5.6. [(Me–NHC–CH_2-Ph)AuC≡CPh] (**2H**)

Yield: 93%, white solid. ^1H NMR ($CDCl_3$, T = 298 K, ppm): δ 3.90 (s, 3 H, NCH_3), 5.42 (s, 2 H, NCH_2), 6.84 (d, 1 H, HC=CH im, J = 1.5 Hz), 6.90 (d, 1 H, CH=CH im, J = 1.5 Hz), 7.18–7.26 (m, 3 H, m/p-phenyl H), 7.31–7.41 (m, 5 H, benzyl H), 7.50–7.53 (m, 2 H, o-phenyl H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, T = 298 K, ppm): δ 37.9 ($N\underline{C}H_3$), 54.6 ($N\underline{C}H_2$), 105.2 (Au$\underline{C}$CPh), 120.2 ($H\underline{C}$=CH im), 122.2 (HC=$\underline{C}$H

Table 4
Crystallographic data.

Compound	**2H**
Formula	$C_{19}H_{17}AuN_2$
M	470.31
Space group	$P2_1/c$
Crystal system	monoclinic
a (Å)	11.3391(2)
b (Å)	10.3526(2)
c (Å)	14.5631(2)
α (°)	90.00
β (°)	90.5976(8)
γ (°)	90.00
U (Å^3)	1709.46(5)
Z	4
T (K)	295
D_{calc} (g cm^{-3})	1.827
$F(000)$	896
μ(Mo Kα) (cm^{-1})	86.04
Measured reflections	19421
Unique reflections	4927
R_{int}	0.0576
Obs. reflections [$I \geqslant 2\sigma(I)$]	3940
θ_{min}–θ_{max} (°)	4.32–30.00
hkl Ranges	−15,15; −14,14; −20,20
$R(F^2)$ (Obs. reflections)	0.0334
$wR(F^2)$ (All reflections)	0.0881
No. Variables	200
Goodness of fit	1.064
$\Delta\rho_{max}$; $\Delta\rho_{min}$ (e Å^{-3})	1.22; −1.81
CCDC Deposition N.	927018

im), 125.5 (AuCCPh), 126.2 (p-phenyl CH), 127.7 (m-phenyl CH), 127.9 (C_{quat} phenyl), 128.5 (benzyl CH), 128.9 (benzyl CH), 132.2(o-phenyl CH), 135.3 (C_{quat} benzyl), 187.6 (NCN). IR (KBr pellet, cm^{-1}): ν = 2925(CH), 2113, 1469(CC), 1592(CN). *Anal.* Calc. for $C_{19}H_{17}AuN_2$: C, 48,52; H, 3,64; N, 5,96. Found: $C_{19}H_{17}AuN_2$: C, 48.43; H, 3.53; N, 5.87%.

4.6. Crystal structure determination

The crystal data of compound **2H** were collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation. The data sets were integrated with the Denzo-SMN package [25] and corrected for Lorentz, polarization and absorption effects (SORTAV) [26]. The structure was solved by direct methods using the SIR97 [27] system of programs and refined using full-matrix least-squares with all non-hydrogen atoms anisotropically and hydrogens included on calculated positions, riding on their carrier atoms.

All calculations were performed using SHELXL-97 [28] and PARST [29] implemented in the WINGX [30] system of programs. The crystal data are given in Table 4.

Appendix A. Supplementary material

CCDC 927018 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.04.026.

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