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FULL PAPER

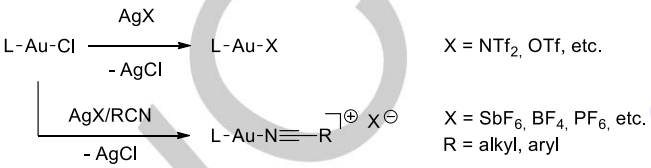
Catalytic Activity of Au(I) Complexes with Hemilabile P,N-Ligands

Bastien Michelet,[a] David Lebœuf,[a] Christophe Bour,[a] Karel Škoch,[b] Filip Horký,[b] Petr Štěpnička*[b] and Vincent Gandon*[a]

Abstract: Two new cationic dinuclear gold(I) complexes, $[Au_2(\mu(P,N)\text{-}\mathbf{5})_2]X_2$, where X = NTf_2 (**7**) or SbF_6 (**8**), containing 2-(diphenylphosphanyl)benzonitrile (**5**) as a P,N-bridging donor have been synthesized and structurally characterized. These air-stable species and their dimeric and polymeric analogues possessing 1'-(diphenylphosphanyl)-1-cyanoferrocene (**1**) as the bridging ligand, $[Au_2(\mu(P,N)\text{-}\mathbf{1})_2](NTf_2)_2$ (**3**) and $[Au(\mu(P,N)\text{-}\mathbf{1})]_n[SbF_6]_n$, were used as pre-catalysts in various Au-mediated C–C and C–O bond forming reactions. The reactivity of these complexed revealed hemilabile nature of their P,N-ligands. In the series of tested pre-catalysts, complex **8** exerted particularly high catalytic activity at low Au loading, even in reactions that usually require high amounts of gold catalyst to proceed efficiently under standard reaction conditions.

Introduction

Organogold(I) complexes have become very popular in synthetic organic chemistry due to their ability to catalyze a myriad of useful transformations. The success of this research area is linked with its close combination with coordination and organometallic chemistry, which aided in finding efficient catalysts and appropriate reaction conditions.[1,2,3] The majority of Au(I) complexes used now as pre-catalysts combine one strongly coordinating monodentate ligand L (phosphines, N-heterocyclic carbenes, etc.) with a weakly coordinating one (typically nitriles and anions such as NTf_2^- and OTf^-).[4] They are usually synthesized by chloride abstraction from the respective [LAuCl] with a silver(I) salt of a weakly coordinating anion (AgX, Scheme 1). The removal of the chloride can be either achieved *in situ* or used to synthesize well-defined catalytically active complexes such as [LAu][NTf_2], [LAu][OTf], or the corresponding nitrile adducts [LAu(RCN)]X.[5]



Scheme 1. Typical synthesis Au(I) pre-catalysts by chloride abstraction.

In spite of the generally high stability of gold(I) pre-catalysts, decomposition may occur during prolonged storage or under reaction conditions.[6] The rapid decay of the active species can be blamed for low turnover numbers, which remain an issue in gold catalysis.[7] Typically, quite high catalyst loadings are required (> 1 mol%), although some large ligands or counterions and silver-free promoters have allowed to circumvent this problem in particular cases.[8]

A stabilization of reactive intermediates can be achieved through the use of hemilabile ligands that combine strongly and weakly coordinating groups in their molecules.[9] The weaker bond between the weakly binding donor moiety and the metal ion can be cleaved by the substrate and formed again once the catalytic product is released from the coordination sphere. Due to chelate effect, the complexes derived from hemilabile ligands are typically more stable than simple solvent adducts. In contrast to other noble metal-based catalysts, the synthesis of Au(I) compounds containing hemilabile ligands (mostly P,N- or carbene,N-donors) has not attracted considerable attention.[10] In fact, the preferred linear geometry of [LAuX] complexes[2h,2i] makes the chelate formation unlikely. On the other hand, the bis(monodentate) coordination mode allowed by hemilabile bifunctional ligands can give rise to Au(I) dimers (Figure 1, **A**) or higher aggregates.[11] These assemblies can be stabilized by aurophilic interactions.[12]

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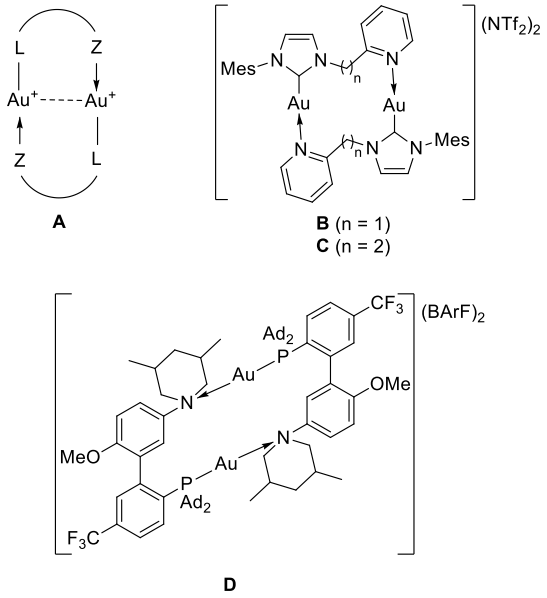
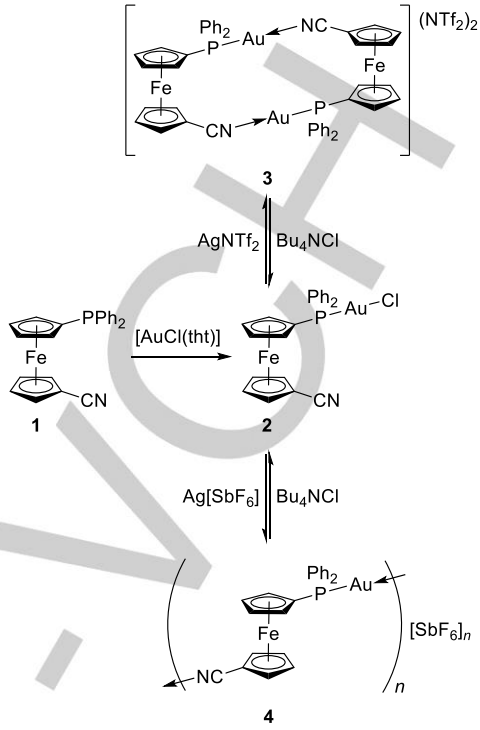


Figure 1. Examples of Au(I) dimers [L = strongly coordinating ligand group (phosphine, NHC, etc.), Z = weakly–coordinating moiety (nitrile, amine, etc.), Mes = mesity, BArF = tetrakis{3,5-bis(trifluoromethyl)phenyl}borate].

Applications of such compounds in catalysis have been only rarely mentioned. For instance, Limbach and coworkers reported that the (NHC,N)Au(I) dimers **B** and **C** are exceptionally active in cycloisomerization of an ω-alkynylfuran, referred to as "problematic" under classical conditions, at Au loading of 0.13 mol%.[10h] Since both gold atoms in these pre-catalysts are coordinatively saturated, it seems clear that the compounds easily split into active monomers under the reaction conditions by dissociation of the Au-N bonds. However, such a dissociation can be difficult, as reported by Zhang *et al*. for complex **D**, which proved to be less active than the corresponding monomeric precursor generated *in situ*.[10k] Hashmi and coworkers also described the deactivation of Au(I) derivatives of P,N-ligands through the formation of aggregates.[13] We have recently used 1'-(diphenylphosphanyl)-1-cyanoferrocene (**1**) as a hybrid P,N-ligand to synthesize various Au(I) complexes (Scheme 2).[10l] Treatment of the phosphane complex [AuCl(**1**-κP)] (**2**) with $AgNTf_2$ led to the symmetrical dimer $[Au(\mu(P,N)\text{-}\mathbf{1})]_2(NTf_2)_2$ (**3**) in which the phosphanylnitrile connects two gold centers as a P,N-bridge (no Au-Au bond was detected). On the other hand, an analogous reaction of **2** with $Ag[SbF_6]$ gave rise to coordination polymer $[Au(\mu(P,N)\text{-}\mathbf{1})]_n[SbF_6]_n$ (**4**). The hemilabile coordination of ligand **1** was confirmed by the reaction with Bu_4NCl which transformed **3** and **4** back into **2**.



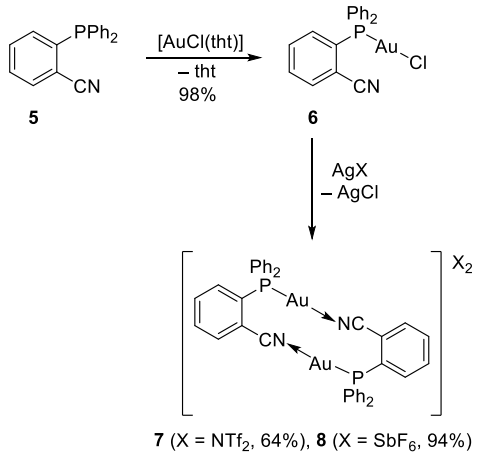
Scheme 2. Synthesis and mutual conversion of Au(I) complexes with phosphanylnitrile **1** (tht = tetrahydrothiophene).

Complexes **3** and **4** are easy-to-handle and air-stable solids, showing no sign of decomposition after weeks when stored in the dark. As pre-catalysts, they were used in low loading for Au(I)-mediated cyclizations of 2-en-4-yn-1-ols into furans (0.01 mol% Au loading for **3**, 0.1 mol% for **4**).[10l] The synthesis of 1,3-oxazoles by Au(I)-catalyzed oxidative cyclization of terminal alkynes with nitriles was also successfully carried out using **3** and **4** (5 mol% Au loading).[10l] In each case, no silver salts were added to activate the complexes, which is appreciable if one considers the negative role that silver can play in gold catalysis.[5b,14] As an extension of our recent work, we describe herein the synthesis of new Au(I) dimers comprising 2-(diphenylphosphanyl)benzonitrile[15] as a P,N-ligand and further explore applications of such species in gold catalysis.

Results and Discussion

Au(I) complexes with 2-(diphenylphosphanyl)benzonitrile

2-(Diphenylphosphanyl)benzonitrile (**5**) reacts with [AuCl(tht)] in the expected manner under the replacement of the weakly coordinating tetrahydrothiophene (tht) ligand to afford phosphine complex **6** (Scheme 2). Subsequent chloride removal with silver(I) salts result in the formation of dinuclear complexes **7** and **8** in which the phosphanylnitrile donor takes up the vacant coordination site and coordinates as a P,N-bridging donor.



Scheme 3. Preparation of Au(I) complexes with 2-(diphenylphosphanyl)-benzonitrile (tht = tetrahydrothiophene).

Complexes **6**-**8** are isolated as colorless solids that are stable to air but should be stored in the dark to prevent decomposition. Their ^{1}H NMR spectra are little informative, only showing complicated multiplets due to the aromatic protons. The ^{31}P NMR spectra of **6**-**8** contain singlet resonances, whose chemical shifts increase in the order **8** < **7** < **6**. The coordination of the nitrile moiety is manifested through a shift of the $\nu_{C\equiv N}$ band in the IR spectra, which is observed at 2225 cm^{-1} for **6** and at 2281 cm^{-1} for both **7** and **8**. The shift of these bands to higher energies upon coordination of the nitrile moiety, observed also in the case of Au(I)-**1** complexes,[10l] points to a low contribution of π-back bonding to the C≡N → Au interaction.[16] Notably the $\nu_{C\equiv N}$ band of the representative dimeric complex **8** shifts to higher energies upon dissolution in dichloromethane (compare 2281 with a shoulder at 2267 cm^{-1} in the solid state with 2306 cm^{-1} in the solution), suggesting that the nitrile group remains coordinated in the solution.

Structure determination carried out for **8** revealed that the compound is a symmetrical dimer in which two phosphanylnitrile ligands coordinate as P,N-bridges between equivalent gold centers. According to a search in the Cambridge Structural Database,[17] structurally characterized compounds featuring *neutral* P,N-donors as bridges between two Au(I) centers are not unprecedented. However, apart for the aforementioned complexes containing 1'-(diphenylphosphanyl)-1-cyanoferrocene as a ligand, they are limited to compounds resulting from various phosphanylated heterocycles and Schiff bases. Thus, in addition to compound **D** (Figure 1), they are represented by the dimers $[Au_2(\mu\text{-}L)_2]X_2$, where L = 2-(dimethylphosphanyl)pyridine, [10a] 2-(diphenylphosphanyl)-*N*-(isopropylidene)aniline,[10b] 2-(diphenylphosphanyl)-1-methylimidazole,[10c] tris(2-isopropyl-1*H*-imidazolyl)phosphane,[18] 9-(2-(diphenylphosphanyl)ethyl)-4,5-diazafluorene,[19] diphenyl(2-imino-3,3-dimethylbutyl)phosphane[20] and 1'-(diphenylphosphanyl)-1-(2-pyridyl)ferrocene[21] (X is usually a simple anion).

The equivalent Au(I) ions in **8** are nearly linearly coordinated (P-Au-N ≈ 173°) and the Au-P and Au-N bond lengths compare well with the parameters reported for **3**[10l] while being slightly longer than those found in the structure of $[AuCl(PPh_3)]$ (Au-P 2.228(1) Å)[22] and $[Au(PPh_3)(MeCN)][SbF_6]$ (Au-P 2.228(1) Å, Au-N 2.038(5) Å).[23] As evidenced by the torsion angle C7-C1-C2-P of 15.2(7)°, the 1,2-disubstituted benzene ring is somewhat twisted, presumably due to the steric demands of the proximal functional groups. The intramolecular Au···Au distance of *ca*. 3.7 Å rules out any in-dimer aurophilic interaction[24] and no significant intermolecular Au···Au contacts were detected in the structure either.

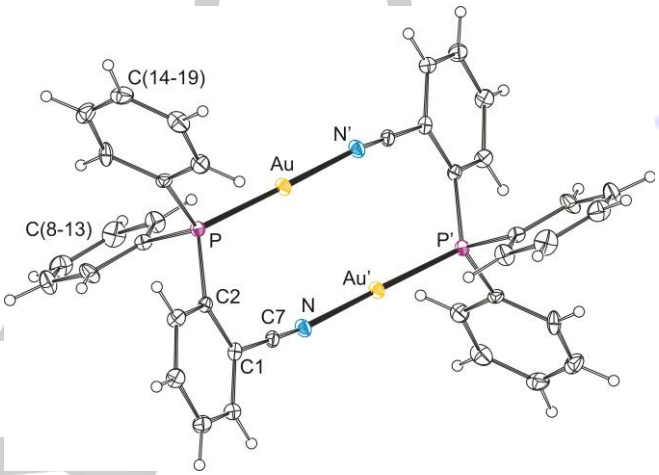
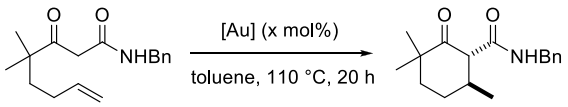


Figure 2. PLATON[25] plot of the complex cation in the structure of **8** with displacement ellipsoids scaled to the 30% probability level. Prime-labeled atoms are generated by crystallographic inversion. Selected distances and angles (in Å and deg): Au-P 2.242(1), Au-N' 2.051(5), Au···Au' 3.7209(6), P-Au-N' 173.1(1), C1-C7-N 177.9(6), C7-N-Au' 156.1(5).

Catalytic evaluation

Complexes **3**, **4**, **7** and **8** were tested as pre-catalysts in various C–C and C–O bond forming reactions. The first of the tested reactions, an intramolecular hydroalkylation of ene-β-ketoamide **9** (Table 1), is typically referred to as a problematic one. Indeed, it requires a prolonged heating in refluxing toluene, which promotes decomposition of the active gold species. Hence, high Au loadings (10 mol%) are required with classical pre-catalyst such as $[(Ph_3P)AuCl]/AgSbF_6$ (entries 1 and 2) as well as with preformed cationic complexes.[8d,g,h,26]

Table 1. Au(I)-Catalyzed Hydroalkylation of Ene-β-Ketoamide **9**.[a]



9 **10** (*dr* 95:5)

Entry	[Au]	x	Conv [%][b]

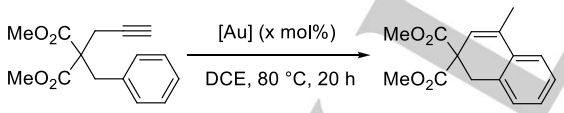
1	[(Ph$_3$P)AuCl]/AgSbF$_6$	1[c]	0
2	[(Ph$_3$P)AuCl]/AgSbF$_6$	10[c]	100 (85)
3	**3**	0.5	77
4	**4**	1	53
5	**7**	0.5	0
6	**8**	0.5	100 (90)
7	**8**	0.05	0

[a] c = 0.2 M. [b] Conversion was determined by ^{1}H-NMR analysis of the crude product. Yield of the isolated product is given in parentheses. [c] x mol% of [(Ph$_3$P)AuCl] and x mol% of AgSbF$_6$.

With 0.5 mol% of **3** (i.e., 1 mol% of Au) or 1 mol% of **4**, full conversion was not reached even after 20 h (entries 3 and 4) and no reaction took place with complex **7** as the pre-catalyst (entry 5). On the other hand, complete and selective transformation of **9** into **10** was achieved with complex **8** (entry 6) with which a very good 90% isolated yield of **10** was obtained at 1 mol% Au loading (= 0.5 mol% of **8**). Lowering the amount of **8** to 0.05 mol% caused the reaction to stop (entry 7). Nevertheless, the excellent result obtained with 0.5 mol% of this catalyst shows that the dissociation of the dimeric precursor (or catalytic activation) is possible even in a weakly coordinating solvent such as toluene. The robustness of the active species also supports the idea of a formation-recombination of the monomers that slows down the decay of the catalyst.

The hydroarylation of arenyne **11** was attempted next (Table 2).[8g,27] This reaction also requires a high temperature to proceed satisfactorily (80 °C in 1,2-dichloroethane). Again, under such conditions, only complex **8** afforded full conversion of **11** into **12**, which was isolated in a 92% yield (entry 5).

Table 2. Au(I)-Catalyzed Hydroarylation of Arenyne **11**.[a]



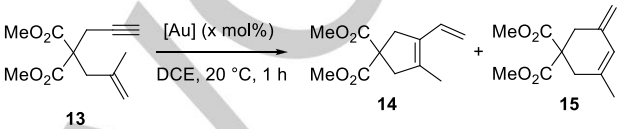
11 **12**

Entry	[Au]	x	Conv [%][b]
1	[(Ph$_3$P)AuCl]/AgSbF$_6$	1	15
2	**3**	0.5	8
3	**4**	1	21
4	**7**	0.5	10
5	**8**	0.5	100 (92)[c]
6	**8**	0.05	0

[a] c = 0.2 M. [b] Conversion was determined by ^{1}H-NMR analysis of the crude product. The yield of the isolated product is given in parentheses. [c] 1 h.

On the other hand, the cycloisomerization of enyne **13**, chosen for a further catalytic evaluation (Table 3), is known to proceed at room temperature, but gives rise to a mixture of isomers, a vinylcyclopentene and a cyclohexene with an exocyclic methylene group.[28]

Table 3. Au(I)-Catalyzed Skeletal Rearrangement of Enyne **13**.[a]



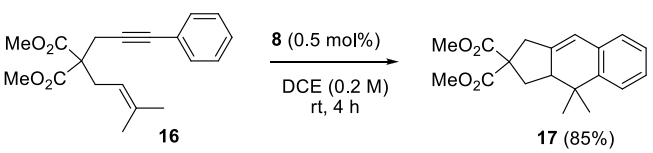
13 **14** **15**

Entry	[Au]	x	**14**:**15**	Conv [%][b]
1	[(Ph$_3$P)AuCl]/AgSbF$_6$	1	-	-[c]
2	**3**	0.5	-	-[c]
3	**4**	1	-	-[c]
4	**7**	0.05	2.5:1	100 (64)[d]
5	**8**	0.05	6.5:1	100 (82)

[a] c = 0.2 M. [b] Conversions were determined by ^{1}H-NMR analysis of the crud product. The yield of the isolated product is given in parentheses. [c] Comple mixture. [d] 3 h.

In the presence of [(Ph$_3$P)AuCl]/AgSbF$_6$, the reaction led to a complex mixture, in which neither **14** nor **15** were observed (entry 1). Complexes **3** and **4** also proved active but unselective catalysts, leading to complex mixtures of products among which **14** and **15** could be identified this time (entries 2 and 3). Gratifyingly, the selectivity improved upon using **7** and **8** (entries 4 and 5). In the latter case, the reaction provided **14** as the major product and the catalyst loading could be lowered to 0.05 mol% Au, with still full conversion and an isolated yield of 82% (entry 5).

The good activity of complex **8** in C–C bond forming reactions was further demonstrated in the formal [4+2] cycloaddition of aryl enyne **16** (Scheme 4).[29] The expected product **17** was isolated in 85% yield after 4 h at room temperature in 1,2-dichloroethane.

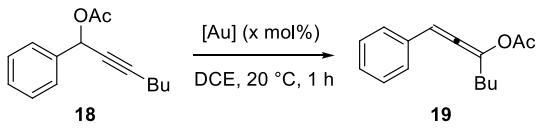


16 **17** (85%)

Scheme 4. Au(I)-Catalyzed [4+2] Cycloaddition of Enyne **16**.

Focusing next on C–O bond forming reactions, the superiority of complex **8** over **3** and **4** was confirmed also for catalytic rearrangement of propargyl acetate **18** to acetoxy allene **19** (in 1,2-dichloroethane at 20 °C, Table 4).[30] Even at a 0.1 mol% Au loading (compared to 1 mol% for **3** and **4**), complex **8** furnished the rearranged product **19** in the highest isolated yield (88%, entry 3).

Table 4. Au(I)-Catalyzed Rearrangement of Propargyl Acetate **18**.[a]



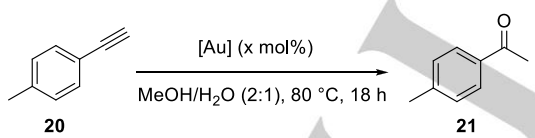
18 **19**

Entry	[Au]	x	Yield [%][b]
1	**3**	0.5	76
2	**4**	1	56
3	**8**	0.05	88

[a] c = 0.2 M. [b] Yield of the isolated product is given.

Complexes **3**, **4**, **7** and **8** seemed virtually equally active when a more strongly coordinating solvent was employed as the reaction medium. When these complexes were applied to hydration of alkyne **20** into ketone **21** in a MeOH/H_2O mixture at 80 °C (Table 5, entries 2-5),[23a, 31] each of these pre-catalysts provided the ketone in a comparably high NMR yield (82-87%). However, in the presence of **8**, the reaction proved to be much faster. Again, the [(Ph_3P)AuCl]/$AgSbF_6$ catalytic mixture was outperformed by these new complexes (entry 1).

Table 5. Au(I)-Catalyzed Hydration of Alkyne **20**.[a]

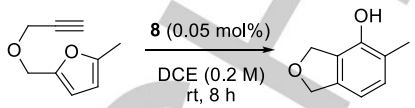


20 **21**

Entry	[Au]	x	Yield [%][b]
1	[(Ph_3P)AuCl]/$AgSbF_6$	1	60
2	**3**	0.5	82
3	**4**	1	87
4	**7**	0.5	85[c],[e]
5	**8**	0.5	86[d],[e]

[a] c = 0.2 M. [b] Determined by ^{1}H-NMR analysis with *p*-anisaldehyde (1 equiv.) as an internal standard. [c] c = 0.5 M, 5 h. [d] c = 0.5 M, 1 h. [e] isolated yields.

Lastly, the cyclization of alkynylfuran **22** into phenol **23** was tested,[32] using only 0.05 mol% of **8** in 1,2-dichloroethane at room temperature (Scheme 5). Even in this case, the desired cyclization product was obtained with a good 70% isolated yield.



22 **23** (70%)

Scheme 5. Au(I)-Catalyzed Phenol Synthesis.

Conclusions

In this study, we have further explored the catalytic activity of a rare type of the dimeric (**3**) and polymeric (**4**) gold(I) complexes derived from 1'-(diphenylphosphanyl)-1-cyanoferrocene ligand. These species showed moderate to low activity and selectivity in the C–C bond forming reactions studied. On the other hand, they efficiently catalyzed C–O bond forming transformations. This family of gold complexes exhibiting hemilabile P,N-ligands was extended by two new dimeric members (**7** and **8**), derived from 2-(diphenylphosphanyl)benzonitrile. Complex **8** proved to be the most versatile pre-catalyst in the series, catalyzing both C–C and C–O bonds at 0.5 mol% and, in some case, even at 0.05 mol% loadings. In particular, **8** proved very robust even at high temperature and in the presence of water. While **8** differs from **7** only by the weaker coordinating nature of its counterion (SbF_6^- vs NTf_2^-), its superiority could be explained by an easier recombination of the two phosphanonitrile gold fragments since the SbF_6^- anion leaves the Au^+ ion free for coordination.
The collected results demonstrate successful implementation of P,N-ligands in gold-catalysis, paving the way for a further catalytic use of these air- and moisture-stable, readily accessible and easy-to-handle complexes.

Experimental Section

General considerations. All manipulations were performed by standard Schlenk techniques under an atmosphere of nitrogen or argon. Compounds **5**,[33] [AuCl(tht)],[34] **9**,[8d] **11**,[35] **13**,[36] **16**,[22b] **18**,[37] and **22**[32e] were prepared according to the literature. Other chemicals were obtained from commercial sources (Sigma-Aldrich, Alfa-Aesar). Dry and deoxygenated dichloromethane was obtained from a PureSolv MD5 solvent purification system (Innovative Technology Inc., Amesbury, USA). Solvents employed during chromatography and work-up were used without any additional purification (reagent grade from Lachner, Czech Republic).

NMR spectra were recorded on Varian UNITY Inova 400 or on Bruker AM250, AV300 or AV360 MHz spectrometers at 25 °C. Chemical shifts are given relative to internal tetramethylsilane (for ^{1}H and ^{13}C NMR) and to external 85% aqueous H3PO4 (for ^{31}P NMR). Electrospray ionization mass spectra (ESI-MS) were obtained with a Bruker Esquire 3000 spectrometer. The samples were dissolved in HPLC-quality methanol. Infrared spectra were measured on a Nicolet Magna 6700 FTIR instrument

in the range 400–4000 cm^{-1}. Elemental analyses were determined with a Perkin-Elmer PE 2400 Series II CHNS/O Elemental Analyzer.

Preparation of [AuCl(5-κ*P*)] (6). A solution of ligand **5** (574.6 mg, 2.0 mmol) in dichloromethane (20 mL) was added to chloro(tetrahydrothiophene)gold(I) (641.2 mg, 2 mmol) dissolved in the same solvent (20 mL). After stirring for 30 min, the clear reaction mixture was filtered through a PTFE syringe filter (0.45 µm pore size) and evaporated under vacuum. The solid residue was taken up with dichloromethane (6 mL) and the solution was added into pentane (60 mL). The precipitated product was isolated by suction, washed with pentane (3× 10 mL) and dried under vacuum. Yield: 1.02 g (98 %), colorless solid.

^{1}H NMR (CD_2Cl_2): δ = 7.07-7.91 (m, $C_6H_4PPh_2$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 30.9 (s) ppm. IR (Nujol): ν_{max} = 3053 m, 2681 w, 2225 m, 1906 w, 1827 w, 1589 w, 1570 w, 1341 w, 1318 m, 1194 w, 1135 w, 1101 s, 1068 w, 1028 w, 998 w, 878 w, 852, 756 m, 766 s, 714 m, 700 s, 693 s, 676 w, 619 w, 581 m, 581 m, 559 m, 546 s, 518 s, 503 s, 479 m, 447 w, 418 w cm^{-1}. ESI+ MS: *m/z* = 542 ([**6** + Na]$^+$). Anal. calc. for $C_{19}H_{14}NAuClP$ (519.7): C 43.91, H 2.72, N 2.70%. Found. C 43.54, H 2.56, N 2.56%.

Synthesis of $[Au_2(\mu(P,N)\text{-}5)_2](NTf_2)_2$ (7). Solid silver(I) bis(trifluoromethanesulfonyl)imide (310.4 mg, 0.80 mmol) weighed on a piece of broken glass was added to solution of **5** (415.7 mg, 0.80 mmol) in dichloromethane (30 mL) and the resulting mixture was stirred for 30 min. A small amount of Celite was added and the mixture was stirred for another 10 min before it was filtered through a syringe filer. The filtrate was diluted with pentane (60 mL) and the mixture was evaporated under vacuum (*N.B.* steps following halogen removal must be carried out as quickly as possible because the solution is highly unstable). The separated product was dried under vacuum and isolated as a colorless solid. Yield: 393 mg (64 %).

^{1}H NMR (CD_2Cl_2): δ = 7.06-7.96 (m, $C_6H_4PPh_2$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 27.4 (s) ppm. IR (Nujol): ν_{max} = 2281 m, 1578 w, 1314 w, 1293 w, 1203 w, 1134 w, 1102 s, 1070 w, 1039 w, 1027 w, 998 m, 967 w, 890 w, 847 w, 799 w, 752 m, 722 m, 703 m, 692 m, 659 s, 617 w, 585 w, 533 m, 507 m, 495 m, 449 w cm^{-1}. ESI+ MS: *m/z* = 502 ([Au(**5**) + H_2O]$^+$), 771 ([Au(**5**)$_2$]$^+$). Anal. calc. for $C_{21}H_{14}N_2AuF_6O_4PS_2$ (764.4): C 32.99, H 1.85, N 3.67%. Found. C 32.82, H 1.84, N 3.49%.

Synthesis of $[Au_2(\mu(P,N)\text{-}5)_2][SbF_6]_2$ (8). Silver(I) hexafluoroantimonate (171.8 mg, 0.50 mmol) weighed on a small piece of broken glass was added to a solution of **5** (259.9 mg, 0.50 mmol) in dichloromethane (20 mL). After stirring for 30 min, the mixture was filtered through a PTFE syringe filter (0.45 µm pore size) and directly added into pentane (80 mL). The separated product was collected on a glass frit, washed with pentane (3× 10 mL) and dried under vacuum. Yield: 340 mg (94 %), colorless solid. Crystals suitable for X-ray diffraction analysis were grown by liquid-phase diffusion of hexane into a dichloromethane solution of the complex.

^{1}H NMR (CD_2Cl_2): δ = 7.26-8.40 (m, $C_6H_4PPh_2$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 23.7 (s) ppm. IR (Nujol): ν_{max} = 2281 m, 2067 sh, 1578 w, 1314 w, 1293 w, 1204 w, 1165 w, 1134 m, 1103 s, 1070 w, 1039 w, 1027 w, 998 w, 971 w, 890 w, 847 w, 800 w, 753 m, 703 w, 692 m, 659 s, 618 w, 585 w, 533 m, 507 w, 495 w, 450 w cm^{-1}. ESI+ MS: *m/z* = 502 ([Au(**5**) + H_2O]$^+$), 771 ([Au(**5**)$_2$]$^+$). Anal. calc. for $C_{19}H_{14}NAuF_6PSb$ (720.0): C 31.69, H 1.96, N 1.95%. Found. C 31.69, H 2.02, N 1.66%.

The physical and spectral data (^{1}H NMR) for the following compounds are in agreement with the data previously reported:

Synthesis of 10. To a solution of **8** (1.4 mg, 0.0010 mmol) in 0.5 mL of toluene was added a solution of ene-β-ketoamide **9** (55 mg, 0.020 mmol) in the same solvent (0.5 mL) and the reaction mixture was stirred at 110 °C for 20 h. Then, the crude product was purified by flash column chromatography using pentane/ethyl acetate (8:2) as the eluent to give pure **10** (49.5 mg, 90%).[8d]

Synthesis of 12. To a solution of **8** (1.4 mg, 0.0010 mmol) in 0.5 mL of 1,2-dichloroethane was added a solution of arenyne **11** (52 mg, 0.020 mmol) in 0.5 mL of 1,2-dichloroethane. The reaction mixture was stirred at 80 °C for 1 h. Following evaporation under vacuum, the crude product was purified by flash column chromatography using pentane/ethyl acetate (9:1) as an eluent to give **12** (48 mg, 92%).[38]

Synthesis of 14 and 15. To a solution of **8** (0.7 mg, 0.0005 mmol) in 2.5 mL of 1,2-dichloroethane was added a solution of enyne **13** (215 mg, 0.960 mmol) in 2.5 mL of 1,2-dichloroethane. The reaction mixture was stirred at room temperature for 1 h. Subsequent evaporation and flash column chromatography using pentane/ethyl acetate (9:1) as the eluent afforded a mixture of **14** and **15** (176 mg, 82%, 6.5:1).[39]

Synthesis of 17. To a solution of **8** (1.5 mg, 0.0011 mmol) in 0.5 mL of 1,2-dichloroethane was added a solution of enyne **16** (66 mg, 0.210 mmol) dissolved in the same solvent (0.5 mL). The reaction mixture was stirred at room temperature for 1 h. The crude product was purified by flash column chromatography using Pentane/EtOAc 9:1 as eluent to give **17** (56 mg, 85%).[22b]

Synthesis of 19. To a solution of **8** (1.2 mg, 0.0008 mmol) in 4 mL of 1,2-dichloroethane was added a solution of propargyl acetate **18** (370 mg, 1.61 mmol) in 4 mL of 1,2-dichloroethane. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was evaporated and the crude product was purified by flash column chromatography using pentane/ethyl acetate (9:1) as the eluent to give **19** (325 mg, 88%).[23d]

Synthesis of 21. To a solution of **8** (6.2 mg, 0.0043 mmol) in 1.8 mL of a MeOH/H_2O (2:1) mixture was added alkyne **20** (100 mg, 0.861 mmol). The reaction mixture was stirred at 80 °C for 1 h. Evaporation followed by flash column chromatography using pentane/ethyl acetate (95:5) as the eluent provided analytically pure **21** (99 mg, 86%).[23a]

Synthesis of 23. To a solution of **8** (1.4 mg, 0.0010 mmol) in 5 mL of 1,2-dichloroethane was added a solution of alkynylfuran **22** (300 mg, 2.0 mmol) in the same solvent (5 mL). The reaction mixture was stirred at room temperature for 8 h. Then, the crude product was purified by flash column chromatography using pentane/ethyl acetate (8:2) as the eluent to afford pure **23** (210 mg, 70%).[31]

Structure determination for 8. $C_{38}H_{28}Au_2F_{12}N_2P_2Sb_2$, M = 1440.0 g mol^{-1}, colorless prism, 0.05 × 0.09 × 0.19 mm^3, monoclinic, space group $P2_1/c$ (no. 14), a = 12.6656(4), b = 6.7301(2), c = 23.5378(7) Å; β = 99.751(1)°; V = 1977.49(1) Å^3, Z = 2, D_{calc} = 2.42 g mL^{-1}.

Full-set diffraction data (±h±k±l) were recorded with a Bruker D8 VENTURE Kappa diffractometer equipped with a PHOTON100 detector, IμS micro-focus sealed tube (Mo Kα radiation, λ = 0.71073 Å) and a Cryostream Cooler (Oxford Cryosystems) at 150(2) K. The data were corrected for absorption (μ = 8.92 mm^{-1}) using a numerical method incorporated in the diffractometer software. A total of 17557 diffractions was recorded (θ_{max} = 27.5°, data completeness = 99.9%), from which 4541 were unique (R_{int} = 2.39%), and 4201 were observed according to the $I > 2\sigma(I)$ criterion.

The structure was solved by direct methods (SHELXT[40]) and refined by full-matrix least-squares routine based on F^2 (SHELXL2014[41]). All non-

hydrogen atoms were refined with anisotropic displacement parameters. The hydrogens were included in their calculated positions and treated as riding atoms with U_{iso}(H) set to 1.2 U_{eq}(C) of their bonding carbon. The refinement converged ($\Delta/\sigma \leq 0.001$, 262 parameters) to R = 3.11% for the observed, and R = 3.52%, wR = 7.57% for all diffractions. The final difference electron density map displayed no peaks of chemical significance, the relatively high extremes ($\Delta\rho_{max}$ = 2.70, $\Delta\rho_{min}$ = –1.60 e Å^{-3}) being attributable to crystal imperfections.

CCDC-1514792 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.

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Keywords: cyclizations • gold • homogeneous catalysis • phosphane ligands • structure elucidation

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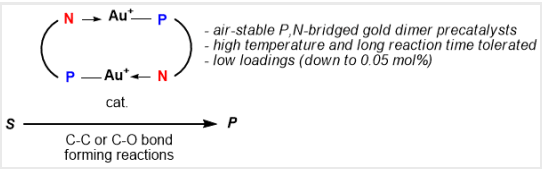

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Catalytic Activity of Au(I) Complexes with Hemilabile P,N-Ligands

Complexes of the type $[Au_2(\mu(P,N)\text{-}L)_2][X]_2$ (X = NTf_2 or SbF_6, L = 1'-(diphenylphosphanyl)-1-cyanoferrocene or 2-(diphenylphosphanyl)benzonitrile) are easy-to-handle and versatile precatalysts for various gold(I)-catalyzed reactions