ChemPubSoc Europe

DOI: 10.1002/chem.201502968

CHEMISTRY A European Journal Full Paper

Homogeneous Catalysis | *Hot Paper*

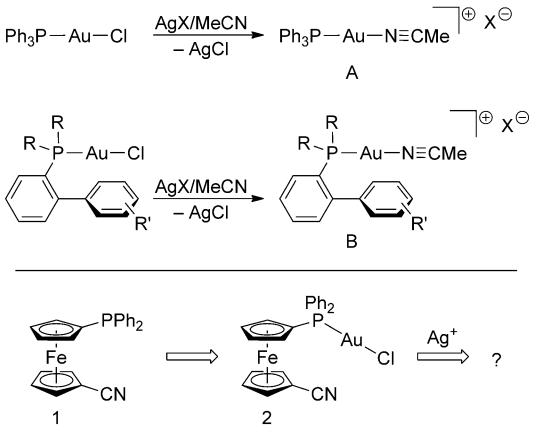
Synthesis and Catalytic Use of Gold(I) Complexes Containing a Hemilabile Phosphanylferrocene Nitrile Donor

Karel Škoch, Ivana Císařová, and Petr Štěpnička*[a]

Abstract: Removal of the chloride ligand from [AuCl(**1**-κ*P*)] (**2**) containing a P-monodentate 1′-(diphenylphosphanyl)-1-cyanoferrocene ligand (**1**), by using silver(I) salts affords cationic complexes of the type [Au(**1**)]X, which exist either as cyclic dimers $[Au(\mathbf{1})]_2X_2$ (**3a**, X = SbF_6; **3c**, X = NTf_2) or linear coordination polymers $[Au(\mathbf{1})]_nX_n$ (**3a′**, X = SbF_6; **3b′**, X = ClO_4), depending on anion X and the isolation procedure. As demonstrated for **3a′**, the polymers can be readily cleaved by the addition of donors, such as Cl^-, tetrahydrothiophene (tht) or **1**, giving rise to the parent compound **2**, [Au(tht)(**1**-κ*P*)][SbF_6] (**5a**) or [Au(**1**-κ*P*)$_2$][SbF_6] (**4a**), respectively, of which the last two compounds can also be prepared by stepwise replacement of tht in [Au(**1**-κ*P*)$_2$][SbF_6]. The particular combination of a firmly coordinated (phosphane) and a dissociable (nitrile) donor moieties renders complexes **3**/**3′** attractive for catalysis because they can serve as shelf-stable precursors of coordinatively unsaturated Au^I fragments, analogous to those that result from the widely used [Au(PR_3)(RCN)]X catalysts. The catalytic properties of the Au-**1** complexes were evaluated in model annulation reactions, such as the synthesis of 2,3-dimethylfuran from (*Z*)-3-methylpent-2-en-4-yn-1-ol and oxidative cyclisation of alkynes with nitriles to produce 2,5-disubstituted 1,3-oxazoles. Of the compounds tested (**2**, **3a′**, **3b′**, **3a**, **4a** and **5a**), the best results were consistently achieved with dimer **3c**, which has good solubility in organic solvents and only one firmly bound donor at the gold atom. This compound was advantageously used in the key steps of annuloline and rosefuran syntheses.

Introduction

Interest in the coordination chemistry[1] of gold has been recently revived, primarily because of rapid developments in the field of homogeneous gold-catalysed reactions.[2] Compounds that are typically employed as catalysts (or catalyst precursors) in gold catalysis are simple $Au^{I/III}$ salts,[2,3] gold–carbene complexes[2,4] and, mainly, stable Au^I phosphane complexes of the type [AuCl(PR_3)], which are typically activated in situ by the removal of the metal-bound halide with Ag^I salts.[2] However, the latter approach can result in the formation of Au–Ag bimetallic systems, the reactivity of which may differ from that of the corresponding Au-only catalyst. This so-called silver effect in gold catalysis has stirred up a vigorous debate[5] and has also prompted a search for defined, silver-free Au^I catalysts.[6] In addition to the very popular use of the solubilizing NTf_2^- counterion,[7] the most successful of these newly introduced compounds appear to be cationic complexes of the type $[Au(PR_3)(RCN)]^+$ with easily dissociated nitrile ligands (e.g., compounds **A** and **B** in Scheme 1),[8,9] which presumably serve as precursors for the catalytically active $(R_3P)Au^+$ species.



Scheme 1.

Recently, we synthesised 1′-(diphenylphosphanyl)-1-cyanoferrocene (**1** in Scheme 1),[10] which can be regarded as a donor-asymmetric[11] analogue of the ubiquitous 1,1′-bis(diphenylphosphanyl)ferrocene (dppf).[12] In view of the unexpectedly versatile coordination behaviour of **1** towards Cu^I,[10] we decided to study the interactions of this ligand with Au^I, the softest Group 11 metal ion.[13] Herein, we describe the synthesis of structurally unique Au^I-**1** complexes (Scheme 1, bottom) and report on their catalytic applications in selected Au^I-mediated organic reactions.

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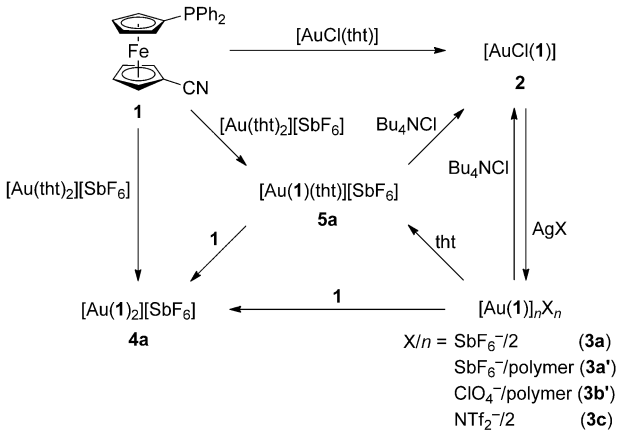
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201502968.

Results and Discussion

Synthesis of the Au^{I} complexes with ligand 1

The syntheses and mutual interconversions of Au^{I} complexes with phosphanylnitrile **1** as a ligand are illustrated in Scheme 2. Ligand **1** reacts cleanly and rapidly with [AuCl(tht)]



Scheme 2. Synthesis and mutual conversions of Au^{I} complexes with phosphanylnitrile **1** (tht = tetrahydrothiophene).

(tht = tetrahydrothiophene) to afford the expected phosphane complex [AuCl(**1**-κ*P*)] (**2**).[14] In the ^{1}H and ^{13}C NMR spectra of **2**, there are characteristic signals assigned to the phosphanylferrocene ligand, whereas the ^{31}P NMR spectrum displays a resonance at $\delta_P = +28.1$ ppm. The crystal structure of **2** (Figure 1) reveals the typical linear coordination around the Au^{I} centre.[15] The ferrocene cyclopentadienyls in P-coordinated **1** are negligibly tilted (the dihedral angle of the cyclopentadienyl planes

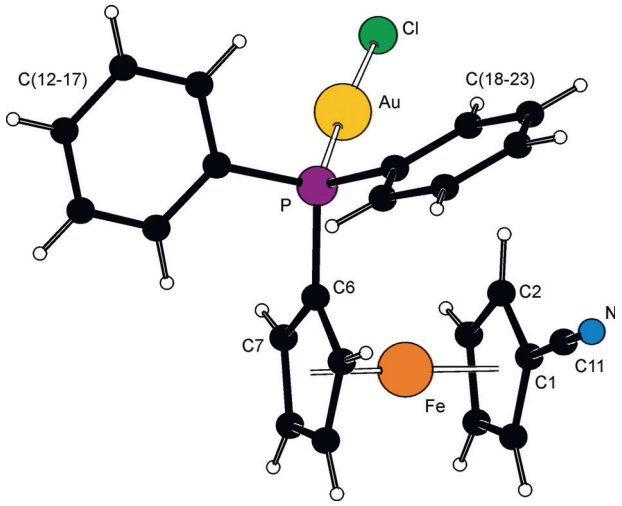


Figure 1. View of the molecular structure of chlorogold(I) complex **2**. Selected bond lengths [Å] and angles [°]: Au–P 2.2287(6), Au–Cl 2.2891(7), C11–N 1.144(4), Fe–Cg1 1.639(1), Fe–Cg2 1.637(1), P-Au-Cl 176.25(2), C1-C11-N 178.8(3).

is only 1.0(2)°) and assume a synclinal eclipsed conformation with a torsion angle of 71.3(2)° for C1-Cg1-Cg2-C6 (τ; see Ref. [12a]; note that Cg1 and Cg2 are the centroids of the cyclopentadienyl rings C(1–5) and C(6–10), respectively). No interactions between the gold atom and the nitrile groups[16] or aurophilic contacts[17] were detected in the solid-state structure of **2**.

Complex **2** reacts smoothly with silver(I) salts to give the corresponding cationic complexes with the general formula [Au(**1**)]$_n$X$_n$ (Scheme 2).[18] Depending on anion X and the isolation procedure (additives) used, these compounds are isolated either as symmetric dimers, in which the phosphanylnitrile connects two gold centres as a P,N-bridge (**3**), or as coordination polymers, in which the ligands play a similar role albeit in an linearly propagating chain (**3′**). For example, the reaction of **2** with Ag[SbF$_6$] gives polymeric [Au(**1**)]$_n$[SbF$_6$]$_n$ (**3a′**). Analogous perchlorate salt **3b′**, obtained in a similar manner, is rather unstable and cannot be crystallised because it readily decomposes. However, the insolubility of **3b′** in common solvents attests to a similar polymeric structure. In contrast, the reaction between **2** and AgNTf$_2$ reproducibly affords the reasonably soluble dimer [Au(**1**)]$_2$(NTf$_2$)$_2$ (**3c**).

The preferred formation of only one type of product under analogous conditions appears to be controlled by an interplay of the relative solubility of the hypothetical Au(**1**)X fragments (as such or solvated) and their overall crystallisation properties. The distinct influence of the synthesis conditions on the aggregation state of the [Au(**1**)]$_n^{n+}$ species can be further highlighted by the serendipitous isolation of complex **3a**,[19] an isomer to **3a′**, in which the structure of the dimeric [Au$_2$(**1**)$_2$]$^{2+}$ motif is associated with two [SbF$_6$]$^-$ anions.[20]

Importantly, the reaction that leads to compounds **3** can be easily reversed by the addition of [Bu$_4$N]Cl as a chloride source (as demonstrated for **3a′**, see Scheme 2). The cleavage of the multi-gold assemblies can be also achieved by the addition of other donors, such as **1**, tht or even a donor solvent (e.g., MeCN). Thus, polymer **3a′** readily dissolves upon the addition of **1** to afford the monogold(I) species [Au(**1**-κ*P*)$_2$][SbF$_6$] (**4a**), in which the two phosphanylnitrile ligands coordinate as equivalent P-monodentate donors.[21] The same product can be prepared directly by the treatment of [Au(tht)$_2$][SbF$_6$] with two equivalents of **1**. A similar reaction at the Au/**1** molar ratio of 1:1 provides a product with an intermediate level of substitution, [Au(**1**-κ*P*)(tht)]SbF$_6$ (**5a**), which can be converted to **4a** by the addition of another equivalent of **1**. Complex **5a** also results from cleavage of polymer **3a′** with tht and can be transformed back to the parent complex **2** upon treatment with [Bu$_4$N]Cl (Scheme 2).

The crystal structures of **3a, 3a′**·Me$_2$CO,[22] **3c** and **4a** were determined by using X-ray diffraction analysis and are presented in Figure 2 and in the Supporting Information.[23,49] Selected geometric parameters are given in Table 1. The Au–P bond lengths in these compounds do not differ greatly from those of parent complex **2**. A slight yet statistically significant elongation of the Au–P bonds in **4a** (compared with complexes **3**/**3′**) can be attributed to steric repulsion of the proximal phosphane moieties. The variation in the lengths of the C≡N bonds

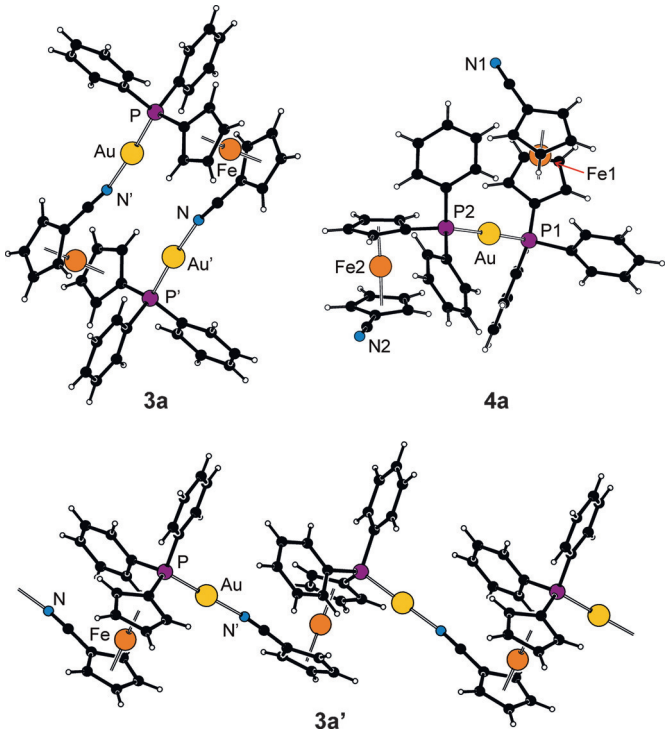


Figure 2. View of the cations in the crystal structures of **3a**, **3a**′·Me_2CO and **4a**. For the conventional displacement ellipsoid plots and structural drawing of **3c**, see the Supporting Information.

Table 1. Comparison of the pertinent geometric parameters of **3a**, **3a**′·Me_2CO, **3c** and **4a**.[a]

	3a	3a′·Me_2CO	3c	4a[b]
bond lengths [Å]				
Au–P	2.225(2)	2.2246(9)	2.232(1)	2.3104(8)/2.3140(8)
Au–N	2.035(4)	2.028(3)	2.035(3)	–
N≡C	1.139(8)	1.143(5)	1.142(5)	1.148(4)/1.136(6)
Fe–Cg1	1.645(3)	1.651(2)	1.645(2)	1.649(1)/1.645(2)
Fe–Cg2	1.642(3)	1.644(2)	1.650(2)	1.648(2)/1.643(1)
angles [°]				
P–Au–N	175.1(1)	179.4(1)	173.4(1)	175.43(2)[c]
Au–N≡C	168.2(5)	173.9(3)	168.0(4)	–
tilt	2.9(4)	3.3(2)	3.4(3)	3.6(2)/4.3(2)
τ	−60.6(5)	−66.8(3)	−78.2(3)	−142.0(2)/75.5(2)

[a] Cg1 and Cg2 are the centroids of cyclopentadienyl rings C1–5 and C6–10, respectively; tilt is the dihedral angle of the cyclopentadienyl planes; τ is the torsion angle of C1-Cg1-Cg2-C6. [b] Data for ligand **1** (Fe1)/ligand **2** (Fe2). [c] P1-Au-P2 angle.

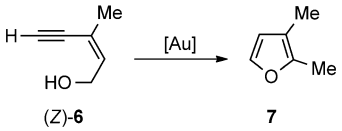
is only marginal (both in the series and with respect to uncoordinated **1**[10]), which indicates that the bonding and back-bonding components of the Au–NC dative bond counteract each other, and thus result in marginal changes in the bond order. This corresponds to a decrease in the ratio between the π-acceptor and σ-donor abilities of the nitrile donors with respect to, for example, the isonitrile and CO ligands.[24] Overall, the Au–donor separations and the interligand angles in compounds **3** and **3**′ are similar to those reported previously for $[Ph_3PAu(NCMe)][SbF_6]$[25] and similar complexes with 2-phosphanylbiphenyl ligands (type **B** in Scheme 1),[25,26] while the Au–P bonds in **4a** compare well with the data determined for complexes $[Au(PR_3)_2]X$, in which R/X = Me/PF_6,[27] Ph/NTf_2,[28] Ph/NO_3[29] and $FcCH_2PPh_2/ClO_4$ (Fc = ferrocenyl).[30]

The conformations of the ferrocene units in complexes **3**/**3**′ are all nearly synclinal eclipsed (ideal value: 72°). One of the two structurally independent molecules of ligand **1** in the structure of **4a** has a similarly compact conformation (Fe2), whereas the other ligand molecule adopts an anticlinal eclipsed conformation, which renders the donor substituents at the ferrocene unit more distant (Fe1).

Catalytic evaluation of the Au-1 complexes

The mutual interconversions of the Au^I complexes with ligand **2** described above clearly demonstrate the hemilabile nature[11] of the cationic Au-**1** species, which results from different strengths of the Au–donor bonds. Apparently, the phosphane donor moiety acts as a firmly bound pivot in these compounds, whereas the CN–Au bond can be readily cleaved by neutral and anionic donors. Such a facile splitting of the parent structure to provide coordinatively unsaturated fragments, and their possible reassembly to allow for self-stabilisation of these intermediates, renders these compounds attractive for use in catalysis.

Catalytic properties of the Au-**1** complexes were evaluated with some known ring-forming reactions;[31] first, in the cyclisation of (*Z*)-3-methylpent-2-en-4-yn-1-ol ((*Z*)-**6**) to 2,3-dimethylfuran (**7** in Scheme 3). In general, this reaction and similar



Scheme 3. Gold-catalysed cycloisomerisation of (*Z*)-**6** to 2,3-dimethyl-furan (**7**).

transformations represent an attractive route to furan derivatives, and although a vast number of transition-metal compounds have been tested in this area,[32] applications of Au^I catalysts to this particular cyclisation of 2-en-4-yn-1-ols still remain quite rare.[33,34]

The results obtained with the Au^I-**1** complexes (Table 2) indicate a superior performance of the **3**-type compounds, which achieve full conversions of (*Z*)-**6** to **7** at catalyst loadings as low as 0.01 %. Even at this scale, the reactions quickly reach completion (being typically complete within less than 5 min) and are strongly exothermic, which becomes evident when the experiments are performed without any solvent and on a larger scale. The best results were obtained with complex **3c**, the solubility of which ensures rapid and complete dissolution of the catalyst in the reaction mixture. However, compounds with two strongly coordinated ligands (phosphane and chloride in **2** and **4a**), and **5a**, proved to be less efficient, which became particularly evident at low metal loadings.[35]

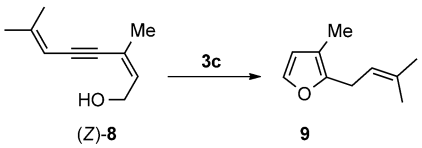
Table 2. Summary of the catalysis results achieved with Au^{I}-**1** complexes in the cyclisation of (*Z*)-3-methylpent-2-en-4-yn-1-ol.[a]

Catalyst	Au loading [%]	Yield [%][b]
[AuCl(tht)]	0.1	82
2	0.1	65
3a′	0.1	quant.
3a′	0.01	45
3b′	0.1	quant.
3b′	0.01	22
3c	0.1	98
3c	0.01	quant.
4a	0.1	0
5a	0.1	quant.
5a	0.01	17
none	0	0

[a] Conditions: reaction in $CHCl_3$ at RT for 30 min. The yields are the average of two independent runs and are given relative to the major (*Z*)-isomer of the starting enynol ((*Z*)/(*E*) ≈90:10). [b] Yield determined by using NMR spectroscopy.

These promising results led us to demonstrate the usefulness of the Au-**1** catalysts under practically relevant conditions. When the cyclisation reaction was carried out with **3c** (0.01 mol%) in the absence of any solvent at a 50 mmol scale (under ambient conditions for 30 min[36]), it afforded furan **7** in an isolated yield of 92% after simple distillation.[37] The turnover frequency (TOF) for catalyst **3c** used in this reaction was as high as 2×10^5 h^{-1}.[38] Unfortunately, a further reduction of the catalyst loading to 0.001 mol% markedly decreased the conversion (only ≈35% **7** was formed at 80 °C over 72 h).

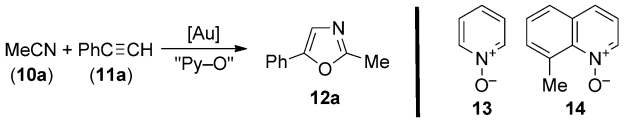
A similar annulation of (*Z*)-3,7-dimethyl-2,6-octadien-4-yn-1-ol (**8**) to give 3-methyl-2-(3-methylbut-2-en-1-yl)furan or rosefuran (**9** in Scheme 4),[39] which is a constituent of natural essential oils,[40] required more forcing conditions, most likely because of the lower reactivity of the internal triple bond present in the substrate. For example, no cyclisation product was detected when neat enynol **8** was treated with **3c** (0.1 mol%) at room temperature for 20 h, whereas heating the reaction mixture to 80 °C for 40 h resulted in only a 4% conversion. On increasing the catalyst amount to 0.5 mol%, however, the reaction proceeded with complete conversion within 2 h at 60 °C and gave pure rosefuran in 91% yield after column chromatography.



(*Z*)-**8** **9**

Scheme 4. Gold-catalysed cycloisomerisation of **8** to rosefuran (**9**).

In a continuation of our catalytic tests, we turned to the synthesis of 1,3-oxazoles[41] by an Au-mediated oxidative cyclisation of alkynes with nitriles in the presence of *N*-heterocyclic *N*-oxides,[42] which offers an attractive alternative to conventional synthetic approaches.[43] The initial screening experiments were carried out with the reaction between acetonitrile and phenylethyne to provide 2-methyl-5-phenyl-1,3-oxazole (**12a** in Scheme 5; the crystal structure of **12a** is presented in the Supporting Information).



Scheme 5. The model Au-catalysed oxidative cyclisation of terminal alkynes with nitriles to give 1,3-oxazoles and structures of the *N*-oxides employed in this reaction.

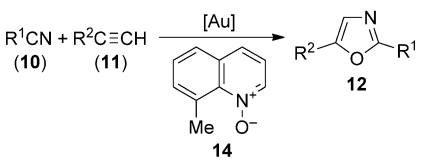
The results (Table 3) clearly differentiated the catalysts. Whereas the coordinatively saturated complexes **2**, **4a** and **5a**, as well the precursor [AuCl(tht)], provided **12a** with only poor yields, compounds **3** performed much better. Similar to the previous tests, the best results were obtained with dimer **3c**, which afforded **12a** in an isolated yield of 78%. A further increase in the yield, though not for all of the complexes (see also the results for practically insoluble **3b′** in Table 3), could be achieved by replacing *N*-oxide **13** with its more bulky counterpart **14**.[42]

Table 3. Summary of catalysis results obtained with various Au^{I} catalysts in the model reaction to give oxazole **12a**.[a]

Catalyst	Yield with *N*-oxide **13** [%]	Yield with *N*-oxide **14** [%]
[AuCl(tht)]	7	n.a.
2	≈1.5	n.a.
3a′	50	83
3b′	33	33
3c	78	88
4a	12	n.a.
5a	44	n.a.

[a] Conditions: phenyl acetylene (0.250 mmol) and *N*-oxide (0.325 mmol, 1.3 equiv) were reacted in the presence of the Au catalyst (5 mol%) in acetonitrile (2.5 mL) at 60 °C for 24 h. The isolated yields are given as the average of two independent runs; n.a. = not available.

The reactions performed next with different substrates (Scheme 6, data in Table 4) demonstrated that the cyclisation of ring-substituted phenylacetylenes with **3c** and **14** in acetonitrile gives the respective 2-methyloxazoles in very good isolated yields. A similar result was attained with propionitrile, but



Scheme 6. Au-catalysed synthesis of 2,5-disubstituted 1,3-oxazoles.

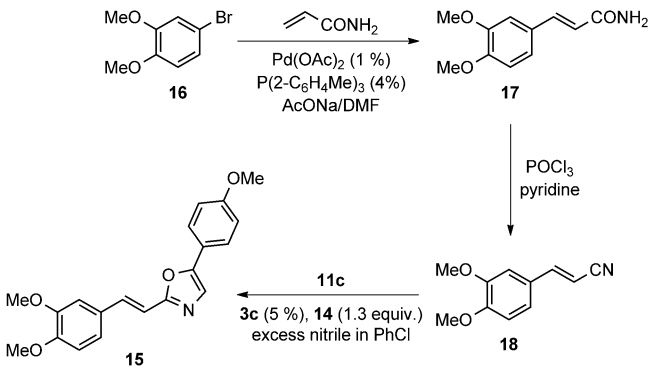
Table 4. The substrate scope tests for the reaction to give oxazoles **12**.[a]

Nitrile	Alkyne	Product	Yield [%]
MeCN (**10a**)	$C_6H_5C{\equiv}CH$ (**11a**)	**12a**	88
10a	4-$MeC_6H_4C{\equiv}CH$ (**11b**)	**12b**	92
10a	4-$MeOC_6H_4C{\equiv}CH$ (**11c**)	**12c**	92
10a	4-$CF_3C_6H_4C{\equiv}CH$ (**11d**)	**12d**	72
10a	4-$BrC_6H_4C{\equiv}CH$ (**11e**)	**12e**	82
EtCN (**10f**)	**11a**	**12f**	85
$CH_2{=}CHCN$ (**10g**)	**11a**	**12g**	46
PhCN (**10h**)[b]	**11a**	**12h**	73

[a] Conditions: alkyne, catalyst **3c** (5 mol%) and **14** (1.3 equiv) were reacted in neat nitrile at 60 °C for 24 h unless specified otherwise. The isolated yields are given as the average of two independents experiments. Note: The first entry is repeated from Table 3 for a comparison. [b] Reaction with the nitrile (6 equiv) in chlorobenzene (2 mL).

the reaction with the generally more reactive acrylonitrile furnished **12g** in only 46% yield.

Encouraged by the successful screening experiments, we set out to employ this [2+2+1] annulation in the preparation of a naturally occurring oxazole alkaloid annuloline (**15**; Scheme 7).[44,45] The nitrile required for this cyclisation, (2*E*)-3-(3,4-dimethoxyphenyl)-2-propenenitrile (**18**), was obtained in



Scheme 7. Synthesis of annuloline **15** by Pd-catalysed cross-coupling and Au-mediated cyclisation.

two steps through a Pd-catalysed Heck coupling of 4-bromoveratrole (**16**) with acrylonitrile and subsequent dehydration of formed amide (*E*)-**17**. The dehydration was associated with a partial isomerisation at the double bond, which led to an approximately 90:10 mixture of the (*E*) and (*Z*) isomers; however, the latter isomer could be easily removed by a single recrystallisation from ethyl acetate/heptane. It is notable that the Heck coupling of **16** with acrylonitrile, which could be suggested as a direct route to nitrile **18**, proved to be less practical due to its lower selectivity (a ≈2:1 mixture of (*E*)- and (*Z*)-**18** was obtained under otherwise similar conditions).

The subsequent cyclisation of **18** with **11c** and *N*-oxide **14** was performed in chlorobenzene with three molar equivalents of the nitrile with respect to **11c** and 5 mol% of **3c** as the catalyst. Gratifyingly, the reaction proceeded smoothly (at 60 °C for 24 h) and provided analytically pure **15** in 63% yield after column chromatography, during which the majority of the unreacted nitrile could also be recovered (2.1 equiv of **18** was isolated). On the whole, this four-step synthesis represents a high-yield and convergent approach towards annuloline (≈34% with respect to **16**) that obviates the use of advanced and/or expensive starting materials and reagents and tedious experimentation, and even avoids unwanted isomerisation at the double bond in the styryl moiety. As such, it represents a practical alternative to the methods reported earlier.[45b,c,46]

In addition to the cyclisation route presented above, another approach to **15** has been investigated based on the Heck coupling of the respective 2-vinyl-1,3-oxazole and **16**.[47d] In a pilot experiment, oxazole **12f** was employed as a model substrate and was treated with **16** in the presence of a Pd catalyst under conventional Heck conditions. However, the reaction did not proceed to any appreciable extent, leading instead to a complete decomposition of the oxazole, whereas **16** remained unchanged.[47]

Conclusion

Abstraction of the chloride ligand from [AuCl(**1**-κ*P*)] (**2**) gives rise to structurally remarkable cationic complexes $[Au(\mathbf{1})]_nX_n$, the degree of association (*n*) of which in the solid state (dimer vs. polymer) can be controlled by the counterion X, presumeably through modulation of the solubility and crystallisation properties of plausible "Au(**1**)X" intermediates. In these compounds, the structurally flexible 1′-(diphenylphosphanyl)-1-cyanoferrocene (**1**) behaves as a bridging hemilabile donor, which makes use of both of its donor moieties.[48] However, the relatively weaker coordination of the nitrile groups allows for an easy disaggregation of these multinuclear compounds upon the addition of donors and thus makes them an attractive and practical source of coordinatively unsaturated Au^I species that are potentially capable of self-stabilisation through equilibria between the mononuclear (solvated) fragments and their aggregated form. The fact that the $[Au(\mathbf{1})]_nX_n$ complexes can indeed serve as a reservoir of catalytically active, low-nuclear gold species was established for selected organic transformations. The catalytic experiments revealed a consistently superior performance of the most soluble derivative, **3c**, in which the dimeric motif $\{Au_2(\mathbf{1})_2\}^{2+}$ pairs with the NTf_2^- anions. This compound, in particular, emerges as an attractive (shelf-stable and well-defined) catalyst for gold-mediated organic reactions, which still rely predominantly on ill-defined species generated in situ from chlorogold(I) complexes with various supporting ligands and silver(I) salts or on the relatively unstable cationic **B**-type complexes.

Acknowledgements

The results presented in this paper were obtained with financial support from the Czech Science Foundation (project no. 13-08890S) and the Grant Agency of Charles University in Prague (project no. 108213).

Keywords: gold · homogeneous catalysis · metallocenes · phosphane ligands · structure elucidation

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[19] Crystals of dimer **3a** formed during the attempted preparation of an asymmetric diphosphane complex (an analogue of **4a**) by the reaction of **3a** with tricyclohexylphosphane and crystallisation from chloroform/diethyl ether.

[20] If the role of the counterion and solid-state effects were negligible, formation of the dimers would be favoured for entropy reasons because the bonds in both compound types ($[Au_2(\mathbf{2})_2]^{2+}$ and $[Au_n(\mathbf{2})_n]^{n+}$) are identical and, thus, no significant contribution from the reaction enthalpy to the overall energy balance would be expected.

[21] The conversion of **2** into **4a** can also be effected through a one-pot reaction by successive addition of **1** and then Ag[SbF$_6$] to a solution of **2**. In this case, however, the product is contaminated by an Ag-**1** complex even when the reaction stoichiometry is strictly maintained.

[22] Crystals of **3a′**·Me$_2$CO suitable for X-ray diffraction analysis were grown by recrystallization from acetone/hexane. However, this solvate partly loses the solvent of crystallization upon drying and prolonged storage.

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Received: July 29, 2015
Published online on September 23, 2015

