ORGANIC CHEMISTRY
FRONTIERS

RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Org. Chem. Front.*, 2015, **2**, 360

Au(I) π-bis(*tert*-butyldimethylsilyl)acetylene triphenylphosphine complex, an effective pre-catalyst for Au(I)-catalyzed reactions†

Dapeng Zhu, Xin Cao and Biao Yu*

Received 19th January 2015,
Accepted 8th February 2015

DOI: 10.1039/c5qo00023h

rsc.li/frontiers-organic

A linear η^2-alkyne π complex of $[Ph_3PAu]^+$, namely Au(I) π-bis(*tert*-butyldimethylsilyl)acetylene triphenylphosphine complex (**1**), was prepared and characterized. The new complex is found to be shelf-stable and effective for a range of the Au(I)-catalyzed alkyne π activation reactions, including a glycosylation reaction with glycosyl *ortho*-alkynylbenzoates as donors.

Introduction

The success of homogeneous gold catalysis with Au(I) complexes, such as $[(L)Au][SbF_6]$ (L = R_3P, NHC, *etc.*), has been testified by numerous alkyne π activation towards nucleophilic attack in assembling structurally complex molecules (Fig. 1A).[1] Among these, we have developed an effective glycosylation protocol employing glycosyl *ortho*-alkynylbenzoates as donors (Fig. 1C);[2a–d] the generality and versatility of this method has been demonstrated in the synthesis of complex oligosaccharides and glycoconjugates.[2] Nevertheless, the loading of the cationic Au(I) complex in these Au(I)-catalyzed reactions is usually ≥10 mol%, due partly to loss of the active Au(I) species *via* disproportionation.[3] In only a few gold-catalyzed reactions high turnover numbers have been achieved,[4] but for the important class of glycosylation reactions such systems have so far not been developed. In this regard, new Au(I) complexes that own better a reactivity-stability balance profile are highly desirable for practical use in the Au(I)-catalyzed reactions.

Among the reported Au(I) coordination complexes,[1] the $[(R_3P)Au(\eta^2\text{-alkyne})][SbF_6]$ pattern (R = alkyl or aryl group) has been suggested as a compelling choice based on several notable merits.[5] The formation of a Au(I) π-[η^2-alkyne] coordination bond could give improved stability to the designed pre-catalysts, for example $[(t\text{-}Bu_3P)Au(\eta^2\text{-alkyne})][SbF_6]$ (alkyne = MeC≡C-*t*-Bu or $Me_3SiC{\equiv}C$-*t*-Bu) (Fig. 1B).[5] In addition, this reversible coordination mode could regulate the release of the active catalytic $Au(I)^+$ species, making the promoting activity of the catalyst in different reactions adjustable. While $[Ph_3PAu]^+$ is one of the most applied gold(I) species for alkyne π activation in Au(I)-catalyzed reactions,[1a–c,5,6] to the best of our knowledge, a linear $[Ph_3PAu]^+$ catalyst in this coordination pattern has not yet been prepared and fully characterized with catalytic activity. Herein, we report a shelf-stable linear η^2-alkyne π complex $[Ph_3PAu]^+$ species, namely Au(I) π-bis(*tert*-butyldimethylsilyl)acetylene triphenylphosphine, and its catalytic activity in the glycosylation reaction and a few other Au(I)-catalyzed reactions.

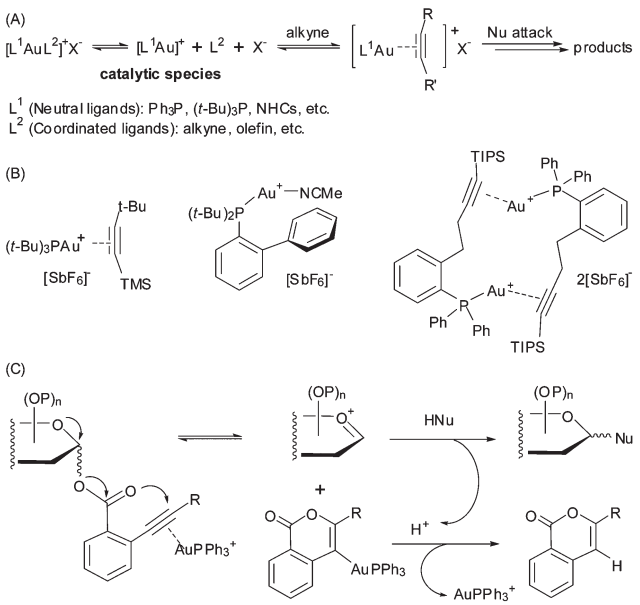


Fig. 1 (A) Au(I)-catalyzed alkyne π activation transformations. (B) Representative $[R_3PAu(\eta^2\text{-alkyne})][SbF_6]$ pattern complexes. (C) The gold(I)-catalyzed glycosidation of glycosyl *ortho*-alkynylbenzoates.

State Key Laboratory of Bio-organic and Natural Products Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China. E-mail: byu@mail.sioc.ac.cn

†Electronic supplementary information (ESI) available. CCDC 1043329. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5qo00023h

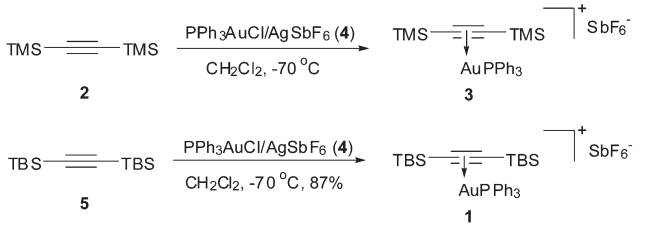
Results and discussion

Preparation of complex 1 and structural characterization

Given the alkyne ligand is activated once coordinated to Au(I) and could thus be readily attacked by nucleophiles, a sterically hindered alkyne is required in preparation of such a stable complex. We first tried to employ TMS-C≡C-TMS (**2**) as the ligand,[7] however, the expected complex **3** made from $PPh_3AuCl/AgSbF_6$ (**4**) was found instable as indicated by the nonuniform ^{31}P signals of the ^{31}P NMR spectra at different temperatures. Thus, acetylene bearing bulky TBS groups, *i.e.*, TBS-C≡C-TBS (**5**),[8] was used as ligand. Upon addition of $PPh_3AuCl/AgSbF_6$ (**4**) into a solution of bis(*tert*-butyldimethylsilyl)acetylene (**5**) in dry CH_2Cl_2 at −70 °C and gradually warming the mixture up to rt, a sharp singlet at 39.0 ppm on ^{31}P NMR showed up, which indicated clearly the formation of a single complex. After removal of the precipitated AgCl, concentration of the filtrate, and recrystallization of the resulting residue from CH_2Cl_2 and hexane (1 : 5) at 0 °C, the desired Au(I) π-bis(*tert*-butyldimethylsilyl) acetylene triphenyl phosphine complex (**1**) was obtained in 87% yield as colourless crystals, which was stable on a shelf for at least half a year (Scheme 1).

The alkynyl carbon signal in complex **1** shifted downfield to 122.8 ppm and turned much wider than those of the free acetylene at 112.9 ppm on ^{13}C NMR spectra. The overlapped signal of the two sp-hybridized carbon atoms demonstrated the existence of an symmetrical Au-[η^2-acetylene] coordination, but not asymmetric bonding, *i.e.*, $\eta^2 \rightarrow \eta^1$ slippage along the alkyne. The ligand's Raman spectra also showed big differences after coordination with an $[AuPPh_3]^+$ species, in which the $\nu_{C\equiv C}$ band signal shifted toward the red end at 1986 cm^{-1} relative to the free ligand peak at 2103 cm^{-1}, which demonstrated the occurrence of the new π coordination.

The X-ray structure of **1** (CCDC 1043329) (Fig. 2) showed an ion-separated complex with perfect symmetrical coordination of the TBS-C≡C-TBS unit to the gold(I) centre intuitively. The $C_1 \equiv C_2$ bond distance of 1.204(7) Å is identical to a typical C≡C bond length of 1.202(5) Å within the limit of error.[5b] Because of the coordination effect of Au(I) as well as the steric hindrance from the PPh_3 group, the two TBS groups bend significantly to the back of the acetylene, leading to the $Si_1–C_1–C_2$ bond angle of 169.3(4)°, so that the C≡C bond is greatly sheltered by the *t*-butylsilyl groups from backside of the molecule. A search of the Cambridge Structural Database[9] reveals that this titled complex is the first example of a linear $[Ph_3PAu]^+$ η^2-alkyne π complex structurally identified by X-ray diffraction.[5]



Scheme 1 Preparation of Au(I) π-[η^2-alkyne] complexes **3** and **1**.

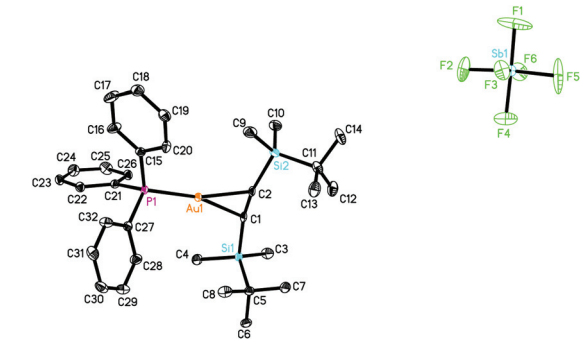
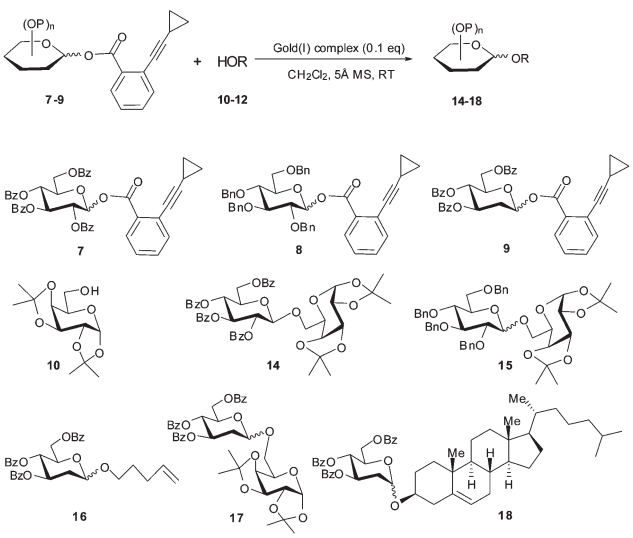


Fig. 2 The X-ray structure of complex **1** (CCDC 1043329). Thermal ellipsoids are at 30% probability; all hydrogen atoms and the solvent of crystallization have been omitted for clarity. Key bond lengths (Å) and angles (°): Au(1)–C(1) 2.226(4), Au(1)–P(1) 2.260(1), C(1)–C(2) 1.204(7); C(15)–P(1)–Au(1) 112.9(1), P(1)–Au(1)–C(1) 164.7(1), Au(1)–C(1)–Si(1) 116.6(2), Si(1)–C(1)–C(2) 169.3(4).

Glycosylation reactions catalyzed by complex 1

With the shelf-stable Au(I) complex **1** in hand, we investigated its catalytic activity in a few representative glycosylation reactions (Scheme 2 and Table 1). Using 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranosyl *ortho*-cyclopropylethynylbenzoate (**7**)[2b] as donor and 1,2;3,4-di-*O*-isopropylidene-D-galactoside (**10**) as acceptor, the condensation in the presence of complex **1** (0.1 eq., CH_2Cl_2, 5 Å molecular sieves (MS), RT) proceeded smoothly, providing the coupled β-disaccharide **14** in nearly quantitative yield (97%; entry 1) within 10 h. In comparison, the completion of a similar reaction with $Ph_3PAuOTf$ (**6**) as the catalyst required 3 h (entry 2). This phenomenon could be rationalized assuming the reversible alkyne→$[Ph_3PAu]^+$ coordination was in action, resulting in a lower concentration of the catalytically active species $[Ph_3PAu]^+$ (than in $Ph_3PAuOTf$) which reduces the rate.

We then explored the catalytic activity of complex **1** in the glycosidation of armed donors, which are more active than



Scheme 2 The Au(I)-catalyzed glycosylation reactions.

Table 1 Glycosylation reactions catalyzed by complex **1**, $Ph_3PAuOTf$ (**6**), or PPh_3AuNTf_2 (**13**)

Entry	Au(I)	Donor	Acceptor	Product	Yield[a] (α/β ratio)[b]
1	**1**	**7**	**10**	**14**	97% (β only)
2	**6**	**7**	**10**	**14**	99% (β only)
3	**1**	**8**	**10**	**15**	92% (α/β = 1.0 : 1)
4	**6**	**8**	**10**	**15**	99% (α/β = 1.2 : 1)
5	**1**	**9**	**11**	**16**	94% (α/β = 6.8 : 1)
6	**13**	**9**	**11**	**16**	95% (α/β = 6.3 : 1)
7	**1**	**9**	**10**	**17**	96% (α/β = 7.4 : 1)
8	**1**	**9**	**12**	**18**	91% (α/β = 13.0 : 1)

[a] Isolated yields. [b] The α/β ratio was determined by ^1H NMR spectroscopic measurements.

those with a participating acyl group at 2-OH (such as **7**). Not surprisingly, coupling of sugar alcohol **10** with 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl cyclopropylethynylbenzoate (**8**) in the presence of complex **1** (0.1 eq., CH_2Cl_2, 5 Å MS, RT) completed within 10 h, providing the coupled glycoside **15** in 92% yield with no stereoselectivity (entry 3).[10] These results are comparable to those obtained with $Ph_3PAuOTf$ (**6**) as the catalyst (entry 4). With 3,4,6-tri-*O*-benzoyl-2-deoxy-D-glucopyranosyl cyclopropylethynyl benzoate **9** as donor,[11,12] the glycosylation of sugar alcohol **10** in the presence of complex **1** led to the coupled disaccharide **17** in excellent yield in favour of the thermodynamically more stable α anomer (α/β = 7.4/1; entry 7). Similar coupling of **9** with the simple alcohol pent-4-en-1-ol (**11**) provided the coupled glycoside **16** in high yield and α selectivity (entry 5). In comparison, similar results were obtained with PPh_3AuNTf_2 (**13**) as the catalyst (entry 6). Again, coupling of the 2-deoxy-sugar donor **9** with cholesterol (**12**) afforded the coupled glycoside **18** in high yield (91%) and excellent α selectivity (α/β = 13 : 1; entry 8).

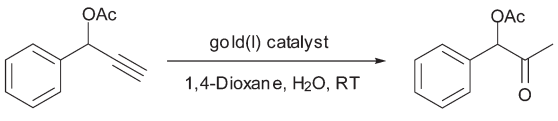
Other reactions catalyzed by complex 1

To further demonstrate the catalytic profile of the Au(I) π-bis-(*tert*-butyldimethylsilyl)acetylene triphenylphosphine complex (**1**), four well documented gold(I)-catalyzed alkyne π activation reactions were examined briefly under the catalysis of complex **1** to compare with the conventional gold(I) pre-catalyst $PPh_3AuCl/AgSbF_6$ (**4**), *i.e.* alkyne hydration,[13] intramolecular rearrangement of alkynyl furan,[14] 1,6-enyne rearrangement,[15] and a tandem 3,3-rearrangement–Nazarov reaction.[16]

Thus, the alkyne substrate **19** in the presence of complex **1** (1 mol%) in wet 1,4-dioxane at RT, was activated and converted smoothly to the corresponding ketone **20** in a satisfactory yield of 93%, which is comparable to the reaction under catalysis of $PPh_3AuCl/AgSbF_6$ (**4**) (1 mol%) (Scheme 3). When the loading of the gold(I) pre-catalyst, either **1** or **4**, was reduced to 0.1 mol %, the hydration of alkyne **19** proceeded sluggishly, leading to 93% recovery of the starting alkyne.

Complex **1** also proved to be effective in promoting the intramolecular conversion of alkynyl furan to phenol (Scheme 3).[14a,b] In the presence of 3 mol% or 1 mol% of the pre-catalyst **1** (CH_2Cl_2, RT), alkynyl furan **21** was converted to

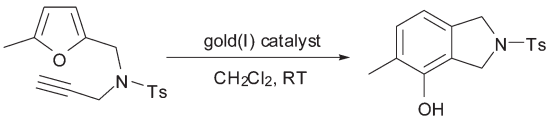
(A) Alkyne hydration



19 20

cat. (mol%)	isolated yield
1 (1%)	93%
4 (1%)	97%

(B) Intramolecular conversion of alkynyl furan to phenol



21 22

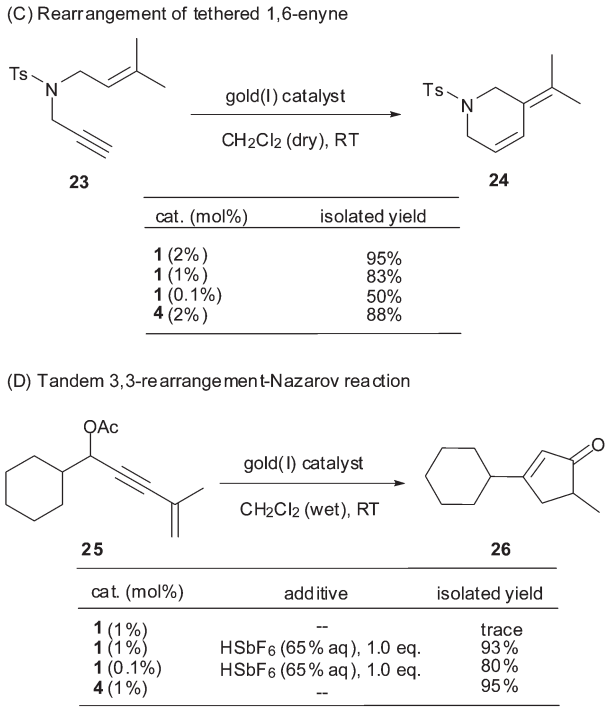
cat. (mol%)	isolated yield
1 (3%)	87%
1 (1%)	67%
4 (3%)	89%

Scheme 3 Complex **1** catalyzed reactions A and B.

the corresponding isoindoline **22** in 87% and 67% yield, respectively. These results demonstrate that complex **1** is comparable or even more effective than the Schmidbaur–Bayler binuclear gold(I) complex ($[(Mes_3PAu)_2Cl]BF_4$), 2.5 mol%, 65% yield) and $PPh_3AuCl/AgSbF_6$ (**4**) (3 mol%, 89%) in this phenol synthesis.

Echavarren *et al.* reported that *N*-propargyl-*N*-isoamylene toluene-4-sulfonylamine **23** underwent endo rearrangement to provide diene **24** in 96% yield under catalysis of $PPh_3AuCl/AgSbF_6$ (**4**) (2 mol%) in dry CH_2Cl_2 at RT (Scheme 4).[15a,b] With 2 mol% of the Au(I) complex **1**, a similar reaction proceeded smoothly to afford diene **24** in 95% yield. When the catalyst loading was decreased to 1 mol% or even 0.1 mol%, the reaction still performed cleanly and afforded the desired product in 83% and 50% (44% starting material recovered) yield, respectively. In this case, the shelf-stable Au(I) complex **1** showed excellent catalytic efficiency comparable to the freshly prepared PPh_3AuSbF_6 (**4**).

Zhang *et al.* reported the preparation of cyclopentenone **26** from enynyl acetate **25** *via* a Au(I)-catalyzed tandem 3,3-rearrangement–Nazarov reaction (Scheme 4).[16] In the presence of Au(I) complex **1** (1 mol%) in wet CH_2Cl_2 at RT, however, we were surprised to find that the conversion of **25** to **26** did not occur at all, whereas a similar transformation proceeded well in the presence of $PPh_3AuCl/AgSbF_6$ (1 mol%) to give cyclopentenone **26** in 95% yield. Our previous studies with a polystyrene-supported Au(I) catalyst showed that a Brönsted acid was crucial to facilitate this reaction.[15c] In fact, upon addition of 1.0 eq. $HSbF_6$ (65% aq.) into the inert mixture of **25** and complex **1** (1 mol%) in CH_2Cl_2 at RT, **26** was obtained smoothly in 93% yield. In comparison, the reaction did not take place in the absence of complex **1**. The present results imply that the release of catalytic $[Ph_3PAu]^+$ from the



Scheme 4 Complex **1** catalyzed reactions C and D.

coordinated complex **1** is much milder than from PPh_3AuCl/$AgSbF_6$ (**4**).

Conclusion

A linear η^2-alkyne π complex of $[Ph_3PAu]^+$, namely Au(I) π-bis-(*tert*-butyldimethylsilyl)acetylene triphenylphosphine complex (**1**), was readily prepared and characterized. This shelf-stable complex **1** is convenient to prepare, store, and handle, while it has been shown to be an effective pre-catalyst for a variety of the Au(I)-catalyzed alkyne π activation reactions, including the glycosidation of *ortho*-alkynylbenzoates, the hydration of alkynes, the intramolecular rearrangement of alkynyl furan, the 1,6-enyne rearrangement, and the tandem 3,3-rearrangement–Nazarov reaction. The mild release of catalytic $[Ph_3PAu]^+$ species in complex **1** might be beneficial in catalyzing certain transformations involving selectivities, and this is a topic of our current interest.

Experimental section

The preparation of complex 1

To a 5 mL flask containing the commercially available TBS-C≡CH (0.5 mL) and dry THF (freshly distilled with Na, 3 mL) was added *n*-BuLi solution (2.5 M in hexane, 1.2 mL) under argon at −15 °C. After stirring for 1 h, a solution of TBSCl (484 mg in 3 mL dry THF) was introduced into the mixture. The mixture was slowly warmed to room temperature and stirred for another 1 h, and was then quenched by H_2O (1 mL). The resulting mixture was extracted with hexane. The organic layer was dried over Na_2SO_4 and concentrated. The residue was recrystallized from MeOH to give the desired compound **5** as a white solid (444.7 mg, 65%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (s, 18H), 0.10 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 112.9, 26.0, 16.5, −4.7; MS-EI$^+$ 197 (100%), 155 (30%), 198 (22%), 199 (9%), 73 (8%), 254 (7%), 141 (6%), 156 (6%); HRMS-EI$^+$ calcd for $C_{14}H_{30}Si_2$ ($[M]^+$) 254.1886, found 254.1885; Raman (532 nm, cm^{-1}) $\nu_{C\equiv C}$ 2103.

A 5 mL flask containing TBS-C≡C-TBS (79.5 mg, 0.31 mmol), PPh_3AuCl (76.5 mg, 0.15 mmol) and $AgSbF_6$ (52.8 mg, 0.15 mmol) was cooled to −70 °C under argon. Then dry CH_2Cl_2 (4 mL, freshly distilled with CaH_2) was introduced *via* a syringe. After stirring for 5 h, the mixture was warmed to room temperature slowly. The resulting AgCl was removed by cotton filtration and the filtrate was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (1 mL) and then hexane (5 mL) was added. The white precipitate was collected to give the desired complex **1** as a white solid (127.9 mg, 87%). The sample for X-ray diffraction analysis was obtained by recrystallization from CH_2Cl_2–hexane *via* vapor diffusion at 0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.55 (m, 9H), 7.49 (dd, J = 13.8, 7.7 Hz, 6H), 1.01 (s, 18H), 0.32 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.8 (d, J = 2.7 Hz), 133.3 (d, J = 2.7 Hz), 130.1 (d, J = 12.3 Hz), 125.9 (d, J = 64.0 Hz), 122.8 (s), 23.9 (s), 16.9 (s), −4.4 (s); ^{31}P NMR (400 MHz, $CDCl_3$) δ 39.0; HRMS (MALDI) calcd $C_{32}H_{45}AuPSi_2$ ($[M - SbF_6]^+$) 713.2457, found 713.2449; Raman (532 nm, cm^{-1}) $\nu_{C\equiv C}$ 1986.

General procedure for the glycosylation reactions (14–18)

To a 25 mL flask containing the donor (0.10 mmol, 1.0 eq.), the acceptor (0.12 mmol, 1.2 eq.) and activated 5 Å molecular sieves (weight equal to the combined weight of the donor and the acceptor), was added dry CH_2Cl_2 to maintain a concentration of 0.05 M under Ar. The gold(I) catalyst **1** (0.0102 mmol, 0.1 eq.) was added 30 minutes later. The mixture was stirred until TLC indicated disappearance of the donor. The molecular sieves were filtered off over Celite and washed with CH_2Cl_2 twice. The filtrate was concentrated under reduced pressure and chromatographed with a gradient of petroleum ether–EtOAc to afford the coupled glycosides (**14–18**).

The hydration of alkyne 19

To a 5 mL Schlenk tube was added a solution of gold(I) catalyst **1** (2.1 mg in 0.5 mL CH_2Cl_2, 0.45 mL), and the solvent was removed under reduced pressure. Then compound **19** (35.5 mg, 2.0 mmol) was added, and the reaction system was protected with Ar. Wet 1,4-dioxane (36 μL H_2O in 1 mL dry 1,4-dioxane, 0.3 mL) was added to the mixture. After stirring for 12 h, the mixture was concentrated *in vacuo*. The residue was chromatographed (petroleum ether–EtOAc, 8 : 1) to yield compound **20** as a colorless oil (36.6 mg, 93%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42–7.39 (m, 5H), 5.98 (s, 1H), 2.19 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 201.59,

170.16, 133.10, 129.30, 129.01, 127.99, 80.87, 26.04, 20.63; MS-EI$^+$ 149 (100%), 107 (96%), 43 (32%), 79 (21%), 77 (14%), 150 (11%), 105 (11%), 108 (10%); HRMS-EI$^+$ calcd for $C_{11}H_{12}O_3$ ([M]$^+$) 192.0786, found 192.0788.

The Hashmi transformation of alkynyl furan 21 to phenol 5-methyl-2-tosylisoindolin-4-ol (22)

To a 25 mL flask containing compound **21** (60.7 mg, 0.2 mmol) and gold(I) catalyst **1** (5.5 mg, 0.006 mmol) was added CH_2Cl_2 (2 mL) at room temperature. After stirring for 1 h, the mixture was concentrated *in vacuo*. The residue was purified by silica gel chromatography (petroleum ether–EtOAc–CH_2Cl_2, 5 : 1 : 1) to give compound **22** as a white solid (52.8 mg, 87%): ^{1}H NMR (400 MHz, d_6-DMSO) δ 8.97 (s, 1H), 7.74 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 6.96 (d, J = 7.6 Hz, 1H), 6.59 (d, J = 7.5 Hz, 1H), 4.49 (s, 2H), 4.46 (s, 2H), 2.36 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, d_6-DMSO) δ 149.8, 143.7, 134.8, 132.9, 130.5, 123.0, 127.4, 123.4, 122.1, 113.3, 53.7, 51.9, 20.9, 15.7; HRMS-ESI$^+$ calcd for $C_{16}H_{17}NO_3SNa$ ([M + Na]$^+$) 326.0821, found 326.0827.

Synthesis of 3-(propan-2-ylidene)-1-tosyl-1,2,3,6-tetrahydropyridine (24) *via* the 1,6-enyne rearrangement of 23

To a 25 mL flask containing compound **23** (54.7 mg, 0.2 mmol) and gold(I) catalyst **1** (3.79 mg, 0.004 mmol) was added dry CH_2Cl_2 (2 mL) at room temperature under Ar. After stirring for 30 minutes, the solution was concentrated *in vacuo*. The mixture was purified by silica gel chromatography (petroleum ether–EtOAc–CH_2Cl_2, 10 : 1 : 1) to give compound **24** as a white solid (52.2 mg, 95%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 6.7 Hz, 2H), 6.34 (d, J = 10.2 Hz, 1H), 5.53 (d, J = 10.0 Hz, 1H), 3.90 (s, 2H), 3.77 (s, 2H), 2.42 (s, 3H), 1.77 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 134.1, 129.9, 129.3, 127.6, 124.5, 122.3, 120.9, 45.03, 45.00, 21.5, 20.3, 19.6; HRMS-ESI$^+$ calcd for $C_{15}H_{19}NO_2SNa$ ([M + Na]$^+$) 300.1029, found 300.1034.

The synthesis of 3-cyclohexyl-5-methylcyclopent-2-enone (26) *via* a tandem 3,3-rearrangement–Nazarov reaction of 25

To a 25 mL flask containing compound **25** (46.3 mg, 0.2 mmol), $HSbF_6$ (~65% aq., 76.5 mg), and gold(I) catalyst **1** (1.86 mg, 0.002 mmol), was added wet CH_2Cl_2 (2 mL) at room temperature. After being stirred for 2 h, the mixture was concentrated *in vacuo*. The residue was purified by silica gel chromatography (petroleum ether–EtOAc, 8 : 1) to give compound **26** as a colorless oil (35.0 mg, 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (s, 1H), 2.85 (dd, J = 18.3, 6.7 Hz, 1H), 2.40 (pd, J = 7.3, 2.4 Hz, 1H), 2.28 (t, J = 11.1 Hz, 1H), 2.19 (d, J = 18.4 Hz, 1H), 1.89 (d, J = 12.6 Hz, 2H), 1.81 (d, J = 12.5 Hz, 2H), 1.73 (d, J = 12.7 Hz, 1H), 1.43–1.19 (m, 5H), 1.17 (d, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.74, 185.52, 126.47, 41.75, 40.35, 38.41, 31.17, 31.14, 25.96, 25.95, 25.90, 16.42. MS-EI$^+$: 178 (100%), 122 (97%), 136 (38%), 107 (37%), 163 (26%), 79 (24%), 95 (20%), 93 (19%); HRMS-EI$^+$ calcd for $C_{12}H_{18}O$ ([M]$^+$) 178.1358, found 178.1356.

Acknowledgements

Financial support from the Ministry of Science and Technology of China (2012ZX09502-002) and the National Natural Science Foundation of China (21432012 and 21102169) is gratefully acknowledged.

Notes and references

1 For selected reviews, see: (*a*) A. S. K. Hashmi and G. J. Hutchings, *Angew. Chem., Int. Ed.*, 2006, **45**, 7896–7936; (*b*) A. Arcadi, *Chem. Rev.*, 2008, **108**, 3266–3325; (*c*) D. J. Gorin, B. D. Sherry and F. D. Toste, *Chem. Rev.*, 2008, **108**, 3351–3378; (*d*) S. Díez-González, N. Marion and S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612–3676; (*e*) Y. Yamamoto, I. D. Gridnev, N. T. Patil and T. Jin, *Chem. Commun.*, 2009, 5075–5087; (*f*) S. P. Nolan, *Acc. Chem. Res.*, 2010, **44**, 91–100; (*g*) A. Fürstner and P. W. Davies, *Angew. Chem., Int. Ed.*, 2007, **46**, 3410–3449; (*h*) A. S. K. Hashmi, *Acc. Chem. Res.*, 2014, **47**, 864–876; (*i*) H. Schmidbaur and A. Schier, *Organometallics*, 2009, **29**, 2–23; (*j*) R. E. M. Brooner and R. A. Widenhoefer, *Angew. Chem., Int. Ed.*, 2013, **52**, 11714–11724.

2 (*a*) Y. Li, Y. Yang and B. Yu, *Tetrahedron Lett.*, 2008, **49**, 3604–3608; (*b*) Y. Li, X. Yang, Y. Liu, C. Zhu, Y. Yang and B. Yu, *Chem. – Eur. J.*, 2010, **16**, 1871–1882; (*c*) Y. Zhu and B. Yu, *Angew. Chem., Int. Ed.*, 2011, **50**, 8329–8332; (*d*) Y. Tang, J. Li, Y. Zhu, Y. Li and B. Yu, *J. Am. Chem. Soc.*, 2013, **135**, 18396–18405; (*e*) Y. Yang, Y. Li and B. Yu, *J. Am. Chem. Soc.*, 2009, **131**, 12076–12077; (*f*) Y. Li, J. Sun and B. Yu, *Org. Lett.*, 2011, **13**, 5508–5511; (*g*) J. Zhang, H. Shi, Y. Ma and B. Yu, *Chem. Commun.*, 2012, **48**, 8679–8681; (*h*) G. Xiao and B. Yu, *Chem. – Eur. J.*, 2013, **19**, 7708–7712; (*i*) J. Yu, J. Sun, Y. Niu, R. Li, J. Liao, F. Zhang and B. Yu, *Chem. Sci.*, 2013, **4**, 3899–3905; (*j*) S. Nie, W. Li and B. Yu, *J. Am. Chem. Soc.*, 2014, **136**, 4157–4160; (*k*) P. Xu, W. Xu, Y. Dai, Y. Yang and B. Yu, *Org. Chem. Front.*, 2014, **1**, 405–414.

3 (*a*) A. S. K. Hashmi, L. Schwarz, J.-H. Choi and T. M. Frost, *Angew. Chem., Int. Ed.*, 2000, **39**, 2285–2288; (*b*) M. Kumar, J. Jasinski, G. B. Hammond and B. Xu, *Chem. – Eur. J.*, 2014, **20**, 3113–3119.

4 (*a*) A. S. K. Hashmi, *Science*, 2012, **338**, 1434–1434; (*b*) M. C. B. Jaimes, C. R. N. Böhling, J. M. Serrano-Becerra and A. S. K. Hashmi, *Angew. Chem., Int. Ed.*, 2013, **52**, 7963–7966; (*c*) M. C. B. Jaimes, F. Rominger, M. M. Pereira, R. M. B. Carrilho, S. A. C. Carabineiroc and A. S. K. Hashmi, *Chem. Commun.*, 2014, **50**, 4937–4940.

5 (*a*) H. V. R. Dias, J. A. Flores, J. Wu and P. Kroll, *J. Am. Chem. Soc.*, 2009, **131**, 11249–11255; (*b*) T. N. Hooper, M. Green, J. E. McGrady, J. R. Patel and C. A. Russell, *Chem. Commun.*, 2009, 3877–3879; (*c*) T. N. Hooper, M. Green and C. A. Russell, *Chem. Commun.*, 2010, **46**, 2313–2315; (*d*) P. P. Sharp, M. G. Banwell, J. Renner, K. Lohmann and A. C. Willis, *Org. Lett.*, 2013, **15**, 2616–

2619; (*e*) N. D. Shapiro and F. D. Toste, *Proc. Natl. Acad. Sci. U. S. A.*, 2008, **105**, 2779–2782; (*f*) D. Zuccaccia, L. Belpassi, L. Rocchigiani, F. Tarantelli and A. Macchioni, *Inorg. Chem.*, 2010, **49**, 3080–3082; (*g*) T. J. Brown and R. A. Widenhoefer, *J. Organomet. Chem.*, 2011, **696**, 1216–1220; (*h*) M. A. Celik, C. Dash, V. A. K. Adiraju, A. Das, M. Yousufuddin, G. Frenking and H. V. R. Dias, *Inorg. Chem.*, 2012, **52**, 729–742; (*i*) A. S. K. Hashmi, T. Lauterbach, P. Nösel, M. H. Vilhelmsen, M. Rudolph and F. Rominger, *Chem. – Eur. J.*, 2013, **19**, 1058–1065.

6 (*a*) C. N. Oberhuber, S. Lopez and A. M. Echavarren, *J. Am. Chem. Soc.*, 2005, **127**, 6178–6179; (*b*) M. Munoz, J. Adrio, J. C. Carretero and A. M. Echavarren, *Organometallics*, 2005, **24**, 1293–1300; (*c*) N. Mézailles, L. Ricard and F. Gagosz, *Org. Lett.*, 2005, **7**, 4133–4136.

7 D. Zhao, A. D. Allen and T. T. Tidwell, *J. Am. Chem. Soc.*, 1993, **115**, 10097–10103.

8 R. West and L. C. Quass, *J. Organomet. Chem.*, 1969, **18**, 55–67.

9 The website of Cambridge Structural Database: http://www.ccdc.cam.ac.uk/pages/Home.aspx.

10 (*a*) A. Demchenko, T. Stauch and G. J. Boons, *Synlett*, 1997, 818–819; (*b*) M. Adinolfi, A. Iadonisi, A. Ravida and M. Schiattarella, *Tetrahedron Lett.*, 2004, **45**, 4485–4488; (*c*) M. A. Oberli, P. Bindschadler, D. B. Werz and P. H. Seeberger, *Org. Lett.*, 2008, **10**, 905–908.

11 (*a*) C. H. Marzabadi and R. W. Frank, *Tetrahedron*, 2000, **56**, 8385–8417; (*b*) D. Hou and T. L. Lowary, *Carbohydr. Res.*, 2009, **344**, 1911–1940; (*c*) J. Park, T. J. Boltje and G. J. Boons, *Org. Lett.*, 2008, **10**, 4367–4370; (*d*) Y. S. Lu, Q. Li, L. H. Zhang and X. S. Ye, *Org. Lett.*, 2008, **10**, 3445–3448.

12 Y. Ma, Z. Li, H. Shi, J. Zhang and B. Yu, *J. Org. Chem.*, 2011, **76**, 9748–9756.

13 (*a*) N. Ghosh, S. Nayak and A. K. Sahoo, *J. Org. Chem.*, 2011, **76**, 500–511; (*b*) D. Wang, R. Cai, S. Sharma, J. Jirak, S. K. Thummanapelli, N. G. Akhmedov, H. Zhang, X. Liu, J. L. Petersen and X. Shi, *J. Am. Chem. Soc.*, 2012, **134**, 9012–9019; (*c*) M. Kumar, G. B. Hammond and B. Xu, *Org. Lett.*, 2014, **16**, 3452–3455.

14 (*a*) A. S. K. Hashmi and J. W. Bats, *J. Am. Chem. Soc.*, 2000, **122**, 11553–11554; (*b*) A. S. K. Hashmi, M. C. Blanco, E. Kurpejović, W. Frey and J. W. Bats, *Adv. Synth. Catal.*, 2006, **348**, 709–713; (*c*) A. S. K. Hashmi, M. Rudolph, H.-U. Siehl, M. Tanaka, J. W. Bats and W. Frey, *Chem. – Eur. J.*, 2008, **14**, 3703–3708; (*d*) Y. Chen, W. Yan, N. G. Akhmedov and X. Shi, *Org. Lett.*, 2010, **12**, 344–347.

15 (*a*) C. N. Oberhuber, M. P. Munoz, E. Bunuel, C. Nevada, D. J. Cardenas and A. M. Echavarren, *Angew. Chem., Int. Ed.*, 2004, **43**, 2402–2406; (*b*) C. N. Oberhuber, M. P. Muñoz, S. López, E. Jiménez-Núñez, C. Nevado, E. Herrero-Gómez, M. Raducan and A. M. Echavarren, *Chem. – Eur. J.*, 2006, **12**, 1677–1693; (*c*) W. Cao and B. Yu, *Adv. Synth. Catal.*, 2011, **353**, 1903–1907.

16 L. Zhang and S. Wang, *J. Am. Chem. Soc.*, 2006, **128**, 1442–1443.