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Synthesis, Structure and Catalytic Activity of a Gold(I) Complex Containing 1,2-Bis(diphenylphosphino)benzene Monoxide

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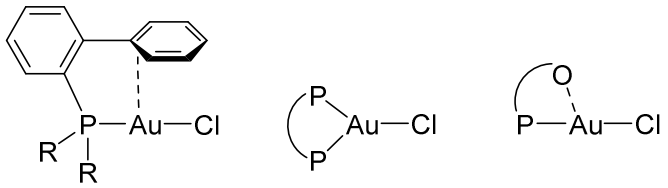
Abstract

The gold(I) complex [Au(dppbO)Cl] was synthesized by reaction of $Na[AuCl_4]\cdot 2H_2O$ with 1,2-bis(diphenylphosphino)benzene (dppb) in the presence of water. This is a new method for the synthesis of a bisphosphine monoxide gold(I) complex. The new gold(I) complex was characterized by NMR spectroscopy and X-Ray crystal structure analysis. In the solid state structure a relatively short contact between the oxygen atom of the phosphine oxide group and the gold center was observed. The catalytic activity of [Au(dppbO)Cl] was tested for three different intermolecular alkyne hydrofunctionalization reactions. Silver tetrafluoroborate was used as co-catalyst for halide abstraction. While the bisphosphine monoxide gold(I) complex showed moderate activity for the hydration of various alkynes and the hydroamination of phenyl acetylene, high activitiy was observed for the hydroarylation of ethylpropiolate. Electron-rich arenes add very fast to the C–C triple bond but with relatively low selectivity.

Introduction

Gold catalysis has become an important methodology for a growing number of organic transformations and for the synthesis of natural products and other complex molecules.[1] In order to use gold catalysis as an efficient synthetic tool, the catalyst structure needs to be tailored for a specific synthetic target. A great variety of gold(I) complexes of the general types [LAuX], [L_2AuX], [(L∩L)Au^IX] or [(L∩L)($Au^I X)_2$] with NHC, NAC, phosphines, bisphosphines, phosphoramides, phosphites, or secondary phosphane oxide ligands has been developed and tested for their catalytic activity.[2] As it was demonstrated with P,N-type ligands, the coordination chemistry of gold(I) center can considerable vary from linear to tricoordinate geometry, while those complexes display mononuclear, trinuclear, or polymeric structures.[2g]



I **II** **III**

It was found that in many cases biphenylylphosphine gold(I) complexes of type **I** show higher catalytic activities than the conventional [R_3PAuCl]-type catalyst (typically R = Ph).[2c,3] For example considerably faster conversion was achieved for the Au^I-catalyzed alkoxycyclization of enynes using biphenylylphosphine ligands.[4a] This can be rationalized by the η^2-interaction of the ortho phenyl group with the gold center. This stabilizing interaction is especially important for the cationic form of complex **I** as it is the actual catalytically active species.[4b,4c]

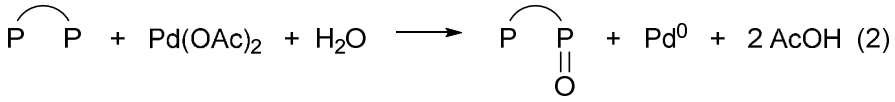
Bisphosphine ligands considerably stabilize the gold(I) center. Complexes of type **II** with bis(diisopropylphosphino)benzene or Xantphos were reported to be superior catalysts comparing

to [R_3PAuCl] (R = Et, Ph).[5] However, bisphosphine gold(I) complexes can also easily form dimeric structures of the type [(L∩L)($Au^IX)_2$], coordination polymers [(L∩L)$Au^IX]_n$, and other more complex structures.[4a,6]

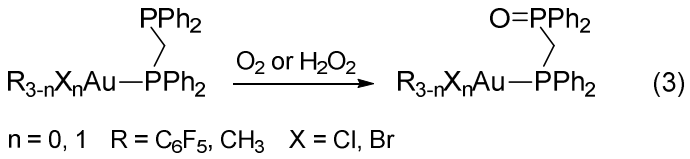
Bisphosphine monoxide gold(I) complexes of type **III** would be an interesting class of new gold(I) catalysts in which the phosphine oxide side of the ligand would contribute to stabilize the gold(I) center, while possibly impacting the substrate activation and reaction path. Bisphosphine monoxide ligands are known as an important class of hemilabile ligands, bearing hard and soft donor functions, which have been used for a number of transition metal catalyzed reactions,[7] e.g. nickel catalyzed ethylene oligomerization.[8] To the best of our knowledge, bisphosphine monoxide gold(I) complexes of type **III** have not yet been studied for their catalytic activity in any organic transformation. So far only two bisphosphine monoxide gold(I) complexes have been reported.[9] In both cases a bisphosphine monoxide ligand was reacted with a gold(I) precursor complex ([NBu_4][$AuBr_2$] or [$Au(SMe_2)_2Cl$]). Bisphosphine monoxide ligands are accessible either by combination of a phosphine oxide with another phosphine fragment,[10] or by Pd-catalyzed selective oxidation of a bisphosphine.[11]

We have now considered a one-pot synthesis for a bisphosphine monoxide gold(I) complex of type **III**, based on (i) the specific redox behavior of $[AuCl_4]^-$ and PPh_3 studied by Roulet et al. (eq. 1)[12] and (ii) the previously described generation of bisphosphine monoxide by selective oxidation of a bisphosphine with palladium acetate in the presence of water (eq. 2).[13]

$$AuCl_4^- + 2\,PPh_3 \longrightarrow AuClPPh_3 + Ph_3PCl_2 + Cl^- \quad (1)$$



In this context it is interesting to note that a bisphoshine coordinated as a monodentate ligand at a gold(III) center can be easily mono-oxidized by air oxygen or hydrogen peroxide (eq. 3).[14,15] However, in these cases the gold center maintains the +3 oxidation state, since external oxidants are used.



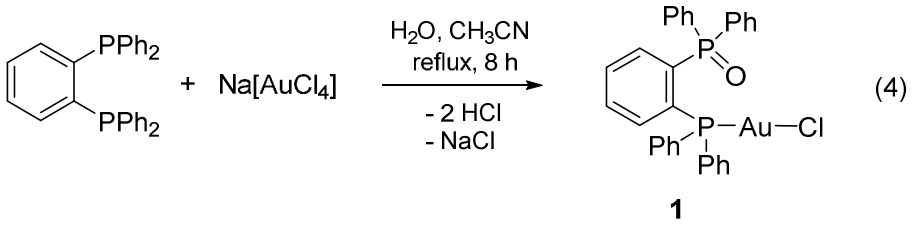
In this paper we report a new synthetic route for a bisphosphine monoxide gold(I) complex [Au(dppbO)Cl] (dppbO = 1,2-bis(diphenylphosphinobenzene) monoxide), its structural characterization, as well as a survey of its catalytic activity for three different alkyne functionalization reactions. We have focused our studies on intermolecular hydration,[3,16] hydroamination,[17] and hydroarylation[18] which have been catalyzed before by gold(I) complexes with various types of phosphine or carbene ligands.

Results and Discussion

Synthesis and Characterization of [Au(dppbO)Cl]

Inspecting reactions eqs 1-3 it was assumed that a bisphosphine could in principle react with a suitable gold(III) precursor to form a bisphosphine monoxide gold(I) complex of type **III**. According to eq 1, one phosphorus atom of the bisphosphine would remain coordinated at the

gold center while the other one would be easily oxidized by Au^{III}. Providing water as oxygen source, as in reaction eq 2, would afford the phosphine oxide. In line with these considerations, $Na[AuCl_4]\cdot 2H_2O$ was reacted with 1,2-bis(diphenylphosphino)benzene (dppb) in a water-acetonitrile solvent mixture. No reaction was observed after stirring the mixture for 24 h at room temperature. However, when the reaction mixture was heated under reflux for 8 h, a white solid slowly precipitated. After evaporation of the solvent, the pale yellow residue was analysed by ^{31}P NMR spectroscopy in acetone-d_6. The spectrum showed a singlet at δ 21.3 and two doublets at δ 30.1 and 34.4 with equal intensity and a ^{31}P-^{31}P coupling constant of 4.8 Hz. The two doublets are in agreement with the new gold(I) complex [Au(dbbzO)Cl] **1** (eq 4), which was unambiguously characterized by X-ray single crystal structure analysis (Fig. 1, see below). The singlet is due to the diphosphine dioxide $dppbO_2$[19] which has formed as a side product. Recrystallization of complex **1** in boiling methanol gave analytically pure complex **1**, which was isolated as a white, air-stable solid. The complex is moderately soluble in acetonitrile, acetone, and dichloromethane, sparingly soluble in diethyl ether and methanol, and insoluble in water.



(4)

1

Suitable crystals for X-ray structure analysis were grown from a saturated solution in acetone. The molecular structure of [Au(dppbO)Cl] **1** is shown in Figure 1, and selected bonding parameters are listed in Table 1. The bisphosphine monoxide coordinates to the gold(I) center as a monodentate ligand. The molecular structure is very similar to that of the two other

bisphosphine monoxide gold(I) complexes mentioned above, containing a dppmO and a chiral phosphanorbonenylphosphine monoxide, respectively.[9] The Au–P bond length of 2.2310(15) Å in complex **1** is similar to that in those other two complexes [2.241(2) and 2.215(1) Å]. Although the non-bonding Au···O contact of 3.057(4) Å in [Au(dppbO)Cl] is significantly shorter than that in the other bisphosphine monoxide gold(I) complexes [3.274 and 3.251 Å], it has the least impact on the linearity of the P–Au–X bond [179.04(6)° vs. 178.53(4)° and 176.1(1)°]. The P=O bond is found to be 1.488(4) Å and is approximately of the same length as that observed in the other two bisphosphine monoxide complexes (1.490(3) and 1.478(3) Å).

The oxygen atom of the phosphine oxide moiety forms two further short intramolecular contacts: to the coordinating phosphorus atom and to the ipso carbon atom C13 of the phosphine group. These contacts are considerably shorter than the respective van der Waals bond lengths (cf. Table 2). The phenyl groups at the ligand periphery are shielding the gold center and thus prevent intermolecular aurophilic contact. Therefore no Au···Au contact was observed in the crystal lattice.

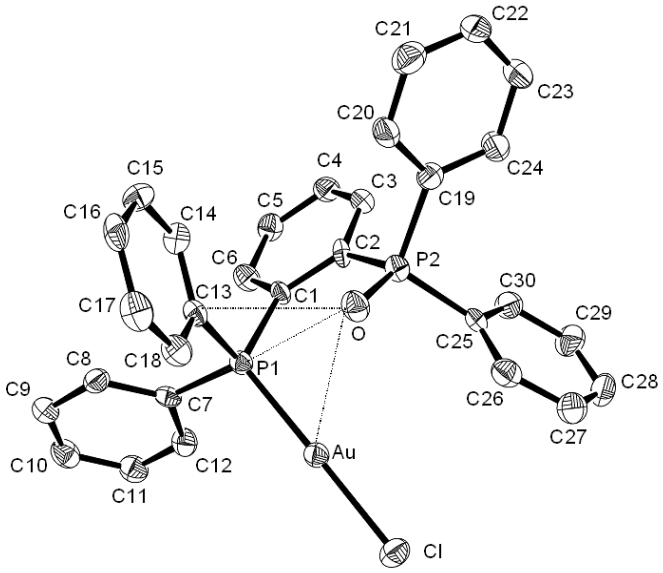


Figure 1 ORTEP drawing of [Au(dppbO)Cl] **1**.

Study of catalytic activity of [Au(dppbO)Cl]

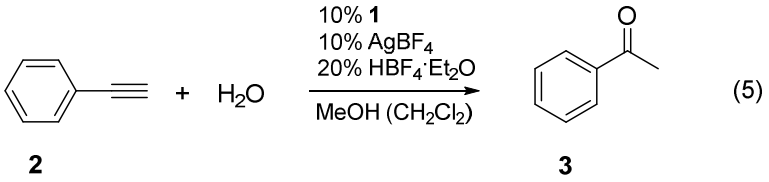
Hydration. The catalytic activity of [Au(dppbO)Cl] was first tested for the hydration of different alkynes. The reaction conditions were chosen similar to those reported by Hashmi et al. for the hydration of phenylacetylene, where nitrogen acyclic carbene (NAC) gold(I) complexes were studied for their catalytic activity.[16n] The results are summarized in Table 3. In the first test run, phenylacetylene **2** was reacted with water in a dichloromethane/methanol solvent mixture in the presence of 10 mol% of [Au(dppbO)Cl] **1**, 10 mol% silver tetrafluoroborate, and 20 mol% tetrafluoroboric acid. After reacting for five days at room temperature, 95% acetophenone **3** was formed (cf. eq 5 and entry 1, Table 3). The same conversion was obtained when phenylacetylene was heated at 80°C for 23 h in a water-methanol mixture with same catalyst and co-catalyst loading (entry 2, Table 3), whereas at room temperature only 20% acetophenone **3** was formed (entry 3, Table 3) over the same period of time. Very little or no conversion occurred with the

gold(I) catalyst by itself or in the presence of only one of the co-catalyst, either silver salt or acid (cf. entries 4-6, Table 3).

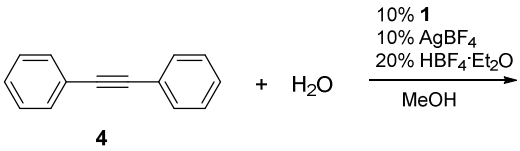
In case of diphenylacetylene **4** only 13% conversion was achieved, and besides the ketone **5**, two alkene derivatives (**6** and **7**) were formed as minor side products (cf. entry 7, eq 6).[20] Aliphatic alkynes (1-hexyne **8** and 2-hexyne **10**) were hydrated under the same conditions very efficiently with nearly complete conversion (cf. eqs 7 and 8 and entries 8 and 9). The regioselectivity of 2-hexyne **10** was found to be relatively poor forming an isomeric ketone mixture of **11** and **12** in a 5:3 ratio.

Using only 1 mol% of [Au(dppbO)Cl] **1** in water/methanol (1:7 ratio) the conversion for the hydration of phenylacetylene **2** was less than 5% (entry 10, Table 3). However when phenylacetylene was reacted in methanol (containing ~1% water), with the same low catalyst load 42% acetophenone **3** was formed together with traces of ether **13** and ketal **14** (eq 9, entry 11).[21]

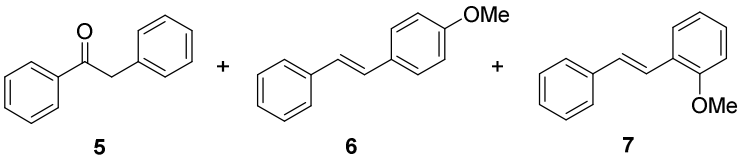
It is interesting to note that in the case of terminal alkynes the reaction solution turned yellow upon addition of the gold(I) catalyst and $AgBF_4$, while the a gray color was observed for internal alkynes. A similar observation of color was reported by Joó and co-workers when a [(NHC)AuCl] complex was reacted with $AgBF_4$ in the presence of phenylacetylene. It is suggested that terminal alkynes form gold(I) alkynyl complexes upon halide abstraction.[16g]



2 **3** (5)

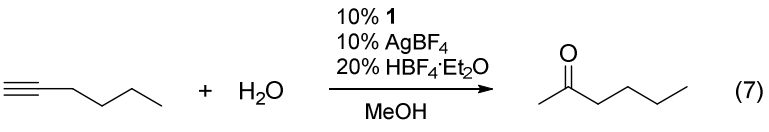


4 (6)

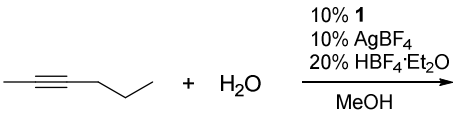


5 **6** **7**

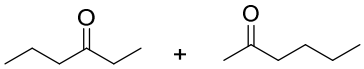
(20 : 3 : 1)



8 **9** (7)

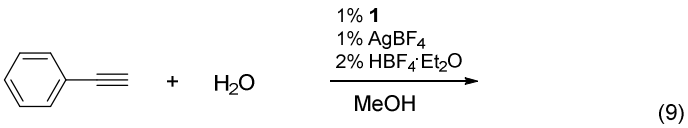


10 (8)

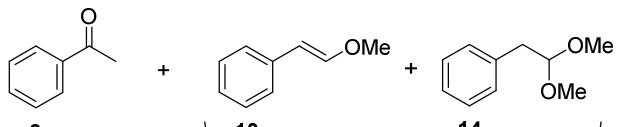


11 **12**

(5 : 3)



2 (9)



3 **13** **14**

42% traces

These results show that [Au(dppbO)Cl] **1**, in combination with silver salt and acid co-catalysts, is in general an active catalyst for the alkyne hydration. The catalytic activity is comparable with that of NAC gold(I) catalysts.[16n] The bisphosphine monoxide gold(I) complex seems to be more active than (IPr)AuCl, MePhosAuCl, and Ph_3PAuCl, however, under Hashmi's conditions $AgSbF_6$ and TFA were used as co-catalysts. The catalytic activity of [Au(dppbO)Cl] is also comparable with that of the (SPhos)gold(I) catalyst systems studied by Leyva and Corma at room temperature.[3] However, in contrast to those catalyst systems, acid co-catalyst is needed for [Au(dppbO)Cl].

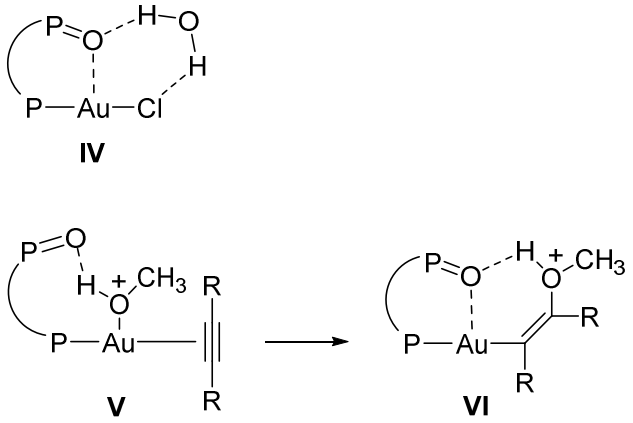
Increasing the temperature from 28 to 80°C the reaction can be substantially accelerated. This has been also demonstrated earlier by Schmidbaur et al. for the hydration of 3-hexyne catalyzed by $[Au(PPh_3)(CO_2C_2F_5)]$ in THF and methanol.[16d]

Aliphatic alkynes are more efficiently hydrated than aromatic alkynes, and there is no substantial difference in reactivity observed between internal and terminal alkynes. This is an interesting fact, since some of the gold catalyst systems reported earlier are very active for terminal alkynes, but much less active or completely inactive for internal alkynes.[16f-16i]

With reducing the catalyst load from 10 to 1 mol% the catalytic activity dropped down from 20 to < 5%. (cf. entries 3 and 10, Table 3). However, when the reaction is performed in ~99%-grade methanol, which corresponds to ca. 3 equiv water per alkyne, 1 mol% of complex **1** even doubles the yield of ketone that was achieved with a 10 mol% catalyst load and large excess of water. Most likely these results are attributed to solubility issues. The excess of water strongly lowers the solubility of the catalyst so that only a small fraction of the original amount is actually available for the reaction. Similar effects were described by Leyva and Corma.[3]

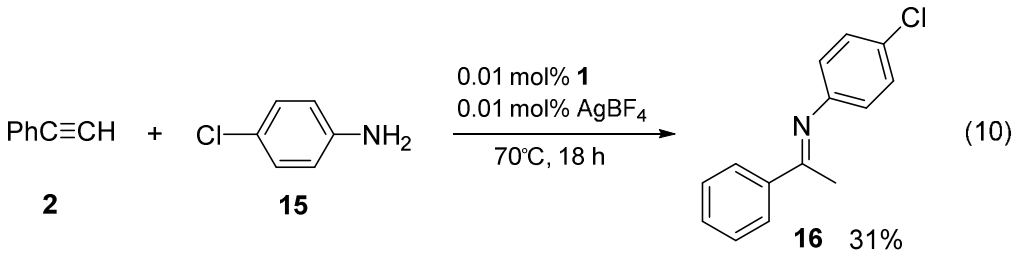
The formation of methoxy species **6**, **7**, **13**, and **14** as by-products in eqs 6 and 9 may indicate methanol addition. However, the given structures (especially **6** and **7** in eq 6) appear very ambiguous due to the detection limits.[20,21] Any isomeric ether or ketal structures would be actually more reasonable. The formation of methyl ether during the hydration of 3-hexyne and in particlar for diphenylacetylene were reported elsewhere.[16f,3,16l] It has been proposed that methanol addition proceeds prior to water addition,[3] and the ketone is actually formed by acid catalyzed hydrolysis of the ketal intermediate.[22]

In the context of the mechanistic considerations, it is interesting to note that the structures of the intermediates for the methanol addition to alkynes, original proposed by Teles[22a] and further studied more in depth by Sicilia[22c] and Hashmi,[22d] will most likely be substantially affected by the hemilabile bisphosphine monoxide ligand. In the solid state structure of a bisphosphine monoxide gold(I) complex hydrogen bonding of a water molecule with the P=O group and the chloro ligand was found (cf. structure **IV** in Scheme 1).[9b] The P=O group may therefore act presumably as proton shuttle and impact the mechanism of the protodeauration step (cf. structures **V** and **VI** in Scheme 1).



Scheme 1 Proposed intermediates for the methanol addition according to Teles.[22]

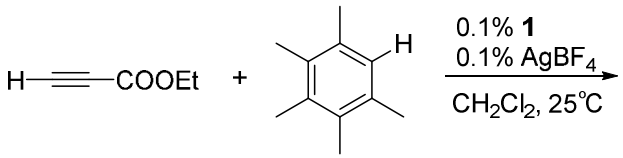
Hydroamination. The hydroamination of phenylacetylene was the second reaction for which the catalytic activity of [Au(dbbpO)Cl] was tested. The reaction conditions were chosen to be similar to those reported by Hayashi and Tanaka who used [Ph_3PAuCH_3] as catalyst.[17a] Interestingly, they have found that electron-deficient aromatic amines are more reactive than the unsubstituted aniline. Thus, 4-chloroaniline **15** was chosen for the test reaction (eq 10).



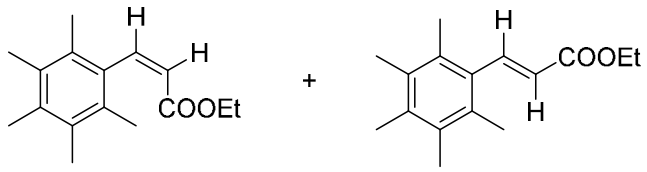
Heating the substrate mixture of phenylacetylene **2** and 4-chloroaniline **15** (1:1 ratio) for 18 h at 70 °C in the presence of 0.01 mol% [Au(dppbO)Cl] **1** and 0.01 mol% of $AgBF_4$ gave a yield of 31% for imine **16**. The reaction was repeated with the same Au-catalyst/$AgBF_4$ loading, but this time 50 mol% of $HBF_4 \cdot Et_2O$ with respect to the substrates was added. This reaction gave a similar yield of imine **16**, however numerous side products were also formed. In this test reaction the bisphosphine monoxide gold(I) complex shows only moderate activity comparing to that reported by Hayashi and Tanaka.[17a] In their case an acid promoter was primarily essential to activate the catalyst [Ph_3PAuCH_3]. Large amounts of acid do not seem to be beneficial for the hydroamination reaction. Gold(I) catalysts of the type [LAuCl] reported by other groups were successfully employed in combination with a silver salt in acid-free reaction medium.[17g,i,j]

It is interesting to note that the P,N-type ligands tested by Stradiotto are particularly efficient for gold(I) catalyzed hydroamination.[17i] It was proposed that the pendant N-donor function of the phosphine ligand plays an active role in proton transfer steps during the catalysis. As pointed out for the alkyne hydration above, the bisphosphine monoxide ligand with its the P=O group can in principle act in the same way. Further experiments are required to explore this particular function of the bisphosphine monoxide ligand, to optimize the reaction conditions, and to explore the substrate scope.

Hydroarylation. Hydroarylation is the third type of intermolecular alkyne functionalization reaction for which the bisphosphine monoxide gold(I) complex was tested. It should be noted that the intermolecular hydroarylation of alkynes has not much been explored by gold catalysis so far, in comparison to hydration and hydroamination.[18] This reaction is more challenging because it is difficult to control the chemo-, regio-, and stereoselectivity. Recently Biffis and co-workers reported an efficient protocol for the hydroarylation of ethylpropiolate under mild conditions using various NHC gold(I) catalysts. [IPrAuCl] showed the highest activity in combination with $AgBF_4$ and acid co-catalysts.[18a] To test the new gold(I) catalyst, [Au(dbbpO)Cl] **1**, the reaction conditions chosen were similar to those reported by Biffis et al., starting with the addition of ethylpropiolate **17** to pentamethylbenzene **18** (eq 11).



17 **18** (11)



19 **20** (traces)

The reaction was performed at room temperature in dichloromethane in the presence of 0.1 mol% [Au(dppbO)Cl] **1**, 0.1 mol% $AgBF_4$, and 1 equivalent of $HBF_4{\cdot}Et_2O$ with respect to the substrates. After only 10 min the reaction was found to be practically complete (entry 1, Table 4) and gave the (*Z*)-alkenylarene **19** with high selectivity. Only traces of (*E*)-isomer **20** were detected. This shows that the bisphosphine monoxide gold(I) complex is even more reactive than the [IPrAuCl]/$AgBF_4$ catalyst. However, in the absence of acid no conversion was observed after 24 h using same load of **1**/$AgBF_4$ (cf. entry 2, Table 4), whereas the NHC gold(I) catalyst still showed some activity under neutral conditions.[18a] In order to see if a reasonable conversion can be achieved with less acid, the reaction was carried out with 10 mol% of $HBF_4{\cdot}Et_2O$ in the presence of 0.1 mol% of complex **1** and 0.1 mol% $AgBF_4$. The reaction was practically complete within <1 h (cf. entry 3, Table 4).

Using these reaction conditions, other arenes were reacted with ethylpropiolate (cf. entries 4-8, Table 4 and Chart 1). When mesitylene and ethylpropiolate was reacted in a 1:1 ratio, the reaction was complete within 30 min and gave a product mixture of mono- and bisalkenylated arenes (**22** and **23**, Chart 1) with 73% and 13% yields, respectively (entry 4). Some traces of **25**, the (*E*)-isomer of the (*Z*)-alkenyl arene **22**, were observed. When half the

amount of mesitylene was reacted with ethylpropiolate (**21** : **17** = 1 : 2), in addition to mono- and bisalkenyl arenes **22** and **23** also the trisalkenylated arene **24** was observed (entry 5). A similar product distribution of mono- and bisalkenylated arenes for the reaction of mesitylene and ethylpropiolate was also obtained by Biffis et al.,[18a] as well as by Reetz and Sommer, who used [R_3PAuCl]/AgX-type catalysts[18b] even though excess arene was employed.

The reaction of 1,3,5-trimethoxybenzene **26** gave (*E*)-alkenylarene **28** as the major product, together with some (*Z*)-isomer **27**, the butadienyl arene **29**, and bisarylalkane **30**. (cf. entry 6, Table 4). The formation of (*E*)-alkenylarene **28** was also observed for the same reaction catalyzed by $AuCl_3$/AgOTf;[18c] whereas the formation of butadienyl arene, which has been a common feature for palladium catalysts,[23] has not been reported so far for any gold catalyzed hydroarylation. Similarly, the bisarylalkane **30** was the only product for the reaction of **17** and **26** with $Pd(OAc)_2$ as catalyst,[23a] but this was not observed with any gold catalyst.

For the reaction of 1,4-dimethoxybenzene the bisarylalkane **34** was obtained as the major product together with the (*Z*)-alkenylarene **32**, as well as other unidentified products (cf. entry 7, Table 4). In contrast to the electron-rich arenes **18**, **21**, **26**, and **31**, naphthalene was a less reactive arene, with which only 52% of the 1-alkenylnaphthalene **36** was obtained after 1.5 h reaction time.

The general trend of reactivity of the different arenes is furthermore illustrated by the reaction of ethylpropiolate with the electron-rich arene 3-methylaniline and the less activated arene cyclohexylbenzene. While 3-methylaniline was extremely reactive under standard conditions (see Table 4, footnote a) with complete conversion of substrates immediately after mixing, cyclohexylbenzene reacted only very slowly (2% conversion). Also the more reactive

the arene, the more side products were formed. This was most pronounced with 3-methylaniline having three available reaction sites.

It should be noted that a characteristic color change was observed during the course of the reaction. The initial light orange-yellow color gradually intensified and turned into a dark brown color as the substrates were being consumed. There was no purple color observed which would indicate catalyst decomposition.

Overall the bisphosphine monoxide gold(I) complex **1** showed a higher catalytic activity for the intermolecular hydroarylation under mild conditions than the NHC gold catalyst reported by Biffis and co-workers. By comparison, Shi and He as well as Reets and Sommer could achieve similar results with higher catalyst load of 5 mol% of the respective gold(I) or gold(III) catalysts, and either longer reaction times or elevated temperatures were needed.[18b,c] However the selectivity of complex **1** depends strongly on the structural and electronic features of the individual arenes.

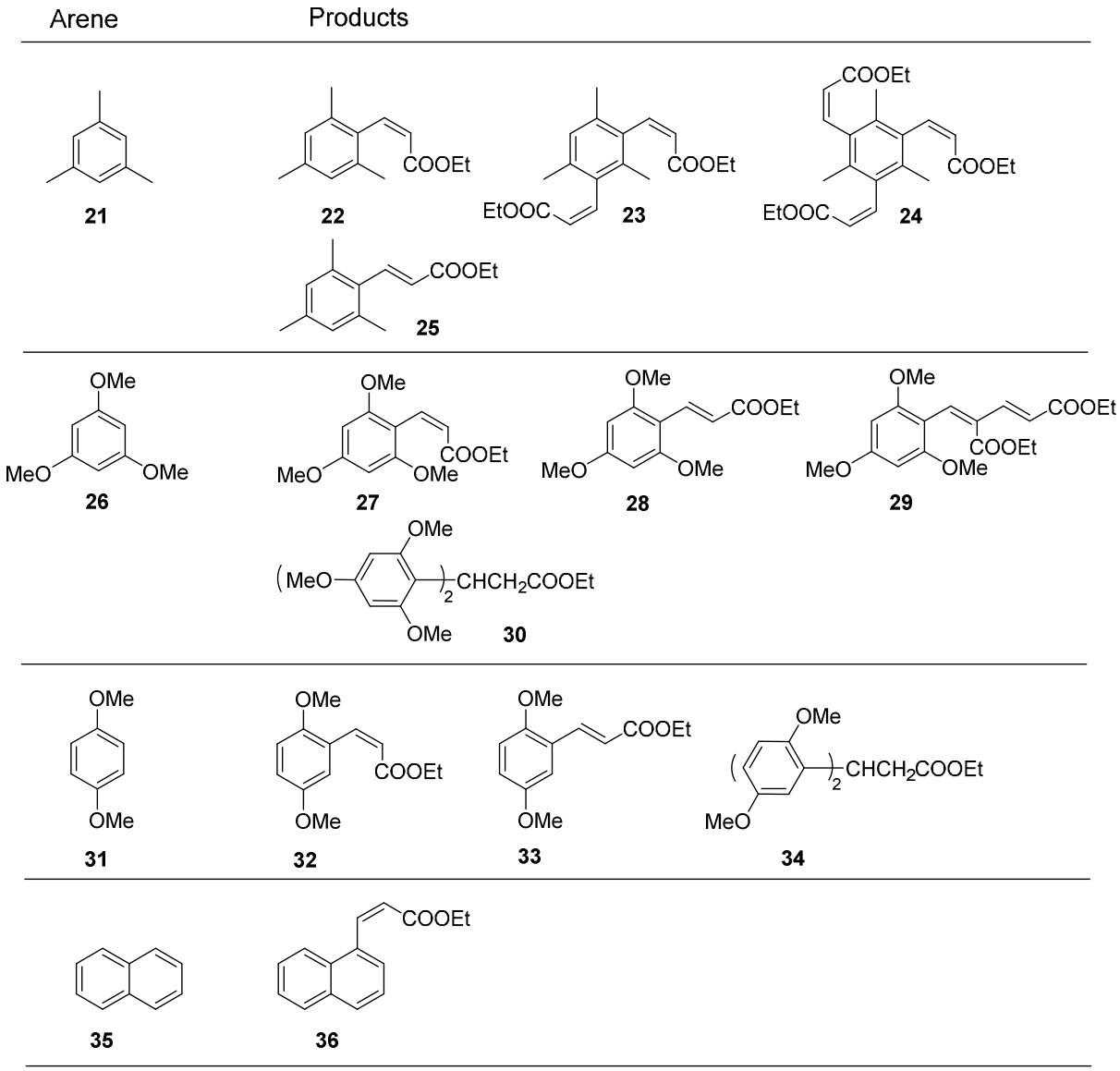


Chart 1 Arenes and hydroarylation products.

Conclusion

In conclusion we have disclosed a new protocol for a simple one-pot synthesis of a bisphosphine monoxide gold(I) complex. The new complex [Au(dppbO)Cl] **1** was structurally characterized by X-ray single crystal analysis. The molecular structure showed that the Au···O

contact of the P=O group with the gold center is the shortest found among the known bisphosphine monoxide gold(I) complexes.

[Au(dppbO)Cl] **1** is the first bisphosphine monoxide containing gold(I) complex tested as a catalyst in organic transformation. While complex **1** shows moderate activity for the hydration and hydroamination of alkynes, it is very active for the hydroarylation under mild conditions and performed better than [IPrAuCl].

Further experiments are in progress to optimize the catalytic alkyne functionalization reactions, and to understand better the reaction mechanisms of the individual reactions and in particular the P=O function of the bisphosphine monoxide. Presumably, this functional group does not only stabilize the gold center but also may actively participate in proton transfer steps. We are also interested whether further derivatives of bisphosphine monoxide gold(I) complexes are accessible by the new synthetic method.

Experimental Section

General. 1,2-Bis(diphenylphosphino)benzene was received from Aldrich and was used without purification. CD_2Cl_2 and acetone-d_6 were received from Aldrich and dried over 3 Å molecular sieves. Sodium tetrachloroaurate(III) dihydrate was commercially available from Strem. The alkynes, arenes, and $HBF_4 \cdot Et_2O$ were received from Aldrich and Alfa Aesar. The alkynes were used without purification. 4-Chloroaniline was recrystallized and the arenes were either distilled or recrystallized before use. The NMR spectra were recorded on Bruker 250, 300 and 400 MHz instruments. The products obtained from the alkyne hydration were analyzed by a

GCMS instrument (Agilent). The ^{1}H NMR shifts were referenced to the resonance of the residual protons of the solvent. The ^{31}P NMR shifts were referenced to external 85% H_3PO_4 standard.

X-Ray Structure Determination of [Au(dppbO)Cl] (1).[24-26] Crystals of complex **1** were grown from a concentrated solution in acetone at room temperature. A suitable crystal was selected, coated in mineral oil, and fixed to a cactus needle which in turn was fashioned to a copper mounting pin. The mounted crystal was placed in a cold nitrogen stream (Oxford) maintained at 110 K. Details of data collection and reduction, and final structure refinement calculation are summarized in Table 5.

A Bruker Smart 1000 X-ray three-circle diffractometer was employed for crystal screening, unit cell determination and data collection. The goniometer was controlled using the SMART software suite (Microsoft operating system). The sample was optically centered with the aid of a video camera such that no translations were observed as the crystal was rotated through all positions. The detector was set at 5.0 cm from the crystal sample (CCD-camera, 512 × 512 pixel). The X-ray radiation employed was generated from a Mo sealed X-ray tube (K_α = 0.71073Å with a potential of 50 kV and a current of 40 mA) and filtered with a graphite monochromator in the parallel mode (175 mm collimator with 0.5 mm pinholes).

Dark currents were obtained for the appropriate exposure time 7 s and a rotation exposure was taken to determine crystal quality and the X-ray beam intersection with the detector. The beam intersection coordinates were compared to the configured coordinates and changes were made accordingly. The rotation exposure indicated acceptable crystal quality and the unit cell determination was undertaken. Fourty five data frames were taken at widths of 0.3° with an exposure time of 10 s. Over 200 reflections were centered and their positions were determined. These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable

cell was found and refined by nonlinear least squares and Bravais lattice procedures and reported. The unit cell was verified by examination of the *hkl* overlays on several frames of data, including zone photographs. No super-cell or erroneous reflections were observed.

After careful examination of the unit cell, a standard data collection procedure was initiated. This procedure consists of collection of one hemisphere of data collected using omega scans, involving the collection over 1400 0.4° frames at fixed angles for ϕ, 2θ, and χ ($2\theta = -28°$, $\chi = 54.73°$), while varying ω. Each frame was exposed for 7 s and contrasted against a 7 s dark current exposure. The total data collection was performed for duration of approximately 9 hours at 110 K. No significant intensity fluctuations of equivalent reflections were observed. All non-hydrogen atoms of the asymmetric unit were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions.

Synthesis of [Au(dppbO)Cl] (1). A round bottom flask was charged with 308 mg (690 μmol) of 1,2-bis(diphenylphosphino)benzene and 250 mg (628 μmol) of $Na[AuCl_4]\cdot 2H_2O$. The reagents were suspended in 10 mL of acetonitrile and 1 mL of water. The reaction mixture was refluxed for 8 hours. The solvent was removed under reduced pressure. The pale yellow solid residue was recrystallized in hot methanol giving a white air-stable solid. Yield: 323 mg (465 μmol, 74%). Mp 255 °C (decomposition). Found C, 52.3; H, 3.9%. $C_{30}H_{24}AuClOP_2$ requires C, 51.9; H, 3.5%. ^{1}H NMR (C_3D_6O, 250 MHz): δ 7.44-7.62 (m), ^{13}C NMR (100.62 MHz, CD_2Cl_2): δ 127.0 (s), 127.1 (s), 127.3 (3), 127.6 (s), 128.2 (d, $J_{C\text{-}P}$ = 3 Hz), 128.3 (d, $J_{C\text{-}P}$ = 2 Hz), 131.4 (s), 131.5 (dd, $J_{C\text{-}P}$ = 3 Hz, $J_{C\text{-}P}$ = 19 Hz), 132.1 (dd, $J_{C\text{-}P}$ = 5 Hz, $J_{C\text{-}P}$ = 9 Hz), 132.6 (s), 132.7 (s), 133.9 (s), 141.8 (s), 142.1 (s). ^{31}P NMR (101.25 MHz, C_3D_6O): δ 34.4 (d, $J_{P\text{-}P}$ = 4.9 Hz), 30.1 (d, $J_{P\text{-}P}$ = 4.8 Hz).

Hydration of alkynes. In a typical catalysis run, a vial was charged with 20 mg (30 μmol) of complex **1,** 6 mg (30 μmol) of $AgBF_4$, 200 μL of H_2O, and 1.4 mL of MeOH. To this mixture 300 μmol of the respective alkyne, 80 μL of n-octane (as internal GC standard), and 8 μL of $HBF_4 \cdot Et_2O$ were added and the mixture was stirred for 23 hours. A 100-μL sample of the reaction mixture was placed into 1 mL of diethyl ether, the solution was filtered through celite and analyzed by GCMS. Conditions were modified for other runs according to Table 3.

Hydroamination of phenylacetylene. A flask was charged with 7 mg (10 μmol) of complex **1**, 2 mg (10 μmol) of $AgBF_4$, 1.1 mL (10 mmol) of phenylacetylene, and 1.3 g of 4-chloroaniline. The mixture was heated to 70 °C for 18 h. A drop of the reaction mixture was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR spectroscopy. In addition to the signals of the imine **16**, those of the starting material appear. The experiment was repeated with the same amounts of catalyst and reagent, but this time 600 μL (5 mmol) of $HBF_4 \cdot Et_2O$ was added.

N-(1-Phenylethylidene)-4-chloroaniline (16): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.18 (s, 3H, CH3), 6.71 (d, $J_{H\text{-}H}$ = 8.2 Hz, C_6H_4Cl), 7.30 (m, 2H, Ph), 7.44 (m, 3H, Ph), 7.93 (d, $J_{H\text{-}H}$ = 8.1 Hz, 2H, C_6H_4Cl).

Hydroarylation of ethylpropiolate. In a typical catalysis run, a Schlenk flask was charged under argon with 7 mg (10 μmol) of complex **1**, 2 mg (10 μmol) of $AgBF_4$, 1 mL (10 mmol) of ethylpropiolate, 10 mmol of arene, and 1 mL of dichloromethane. To the mixture 122 μL of $HBF_4 \cdot Et_2O$ was added. The mixture was stirred under argon at room temperatures for about 1 h. Conditions were modified for other runs according to Table 4. The course of reaction was followed by sampling a drop about every 10 min from the reaction mixture, which was analyzed by ^{1}H NMR spectroscopy. The hydroarylation products were identified based on the chemical shifts reported for earlier in literature.[18b,18c,23a]

Ethyl (*Z*)-3-(Pentamethylphenyl)propenoate (19): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.13 (t, $J_{H\text{-}H}$ = 7.2 Hz, 3H, CH_2CH_3), 2.17 (s, 6H, CH_3), 2.23 (s, 6H, CH_3), 2.26 (s, 3H, CH_3), 4.06 (q, $J_{H\text{-}H}$ = 7.1 Hz, 2H, CH_2CH_3), 6.17 (d, $J_{H\text{-}H}$ = 12.0 Hz, 1H, =CH), 7.17 (d, $J_{H\text{-}H}$ = 12.0 Hz, 1H, =CH).

Ethyl (*E*)-3-(Pentamethylphenyl)propenoate (20):[27] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.36 (t, $J_{H\text{-}H}$ = 7.2 Hz, 3H, CH_2CH_3), 2.29 (s, 3H, CH_3), 4.30 (q, $J_{H\text{-}H}$ = 7.1 Hz, 2H, CH_2CH_3), 5.92 (d, $J_{H\text{-}H}$ = 16.3 Hz, 1H, =CH), 7.93 (d, $J_{H\text{-}H}$ = 16.5 Hz, 1H, =CH).

Ethyl (*Z*)-3-Mesitylpropenoate (22): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.15 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H, CH_2CH_3), 2.18 (s, 6H, CH_3), 2.25 (s, 3H, CH_3), 4.08 (q, $J_{H\text{-}H}$ = 7.1 Hz, 2H, CH_2CH_3), 6.13 (d, $J_{H\text{-}H}$ = 11.7 Hz, 1H, =CH), 6.89 (s, 2H, aryl-H), 7.05 (d, $J_{H\text{-}H}$ = 11.7 Hz, 1H, =CH).

Diethyl (*Z*)-3,3'-(2,4,6-Trimethyl-1,3-phenylene)bis(propenoate) (23): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.17 (t, $J_{H\text{-}H}$ = 7.2 Hz, 6H, CH_2CH_3), 2.06 (s, 3H, CH_3), 2.16 (s, 6H, CH_3), 4.19 (q, $J_{H\text{-}H}$ = 7.0 Hz, 4H, CH_2CH_3), 6.17 (d, $J_{H\text{-}H}$ = 11.8 Hz, 2H, =CH), 6.97 (s, 1H, aryl-H), 7.08 (d, $J_{H\text{-}H}$ = 11.8 Hz, 2H, =CH).

Triethyl (*Z*)-3,3',3"-(2,4,6-Trimethyl-1,3,5-phenylene)tris(propenoate) (24):[27] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.20 (d, $J_{H\text{-}H}$ = 11.8 Hz, 2H, =CH), 7.14 (d, $J_{H\text{-}H}$ = 11.8 Hz, 2H, =CH).

Ethyl (*E*)-3-Mesitylpropenoate (25):[27] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.60 (d, $J_{H\text{-}H}$ = 16.1 Hz, 1H, =CH), 7.88 (d, $J_{H\text{-}H}$ = 16.1 Hz, 1H, =CH).

Ethyl (*Z*)-3-(2,4,6-trimethoxyphenyl)propenoate (27):[27] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.60 (d, $J_{H\text{-}H}$ = 12.0 Hz, 1H, =CH), 6.83 (d, $J_{H\text{-}H}$ = 12.0 Hz, 1H, =CH).

Ethyl (*E*)-3-(2,4,6-trimethoxyphenyl)propenoate (28): ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32 (t, $J_{H\text{-}H}$ = 7.2 Hz, 3H, CH_2CH_3), 3.85 (s, 3H, OCH_3), 3.87 (s, 6H, OCH_3), 4.24 (q, $J_{H\text{-}H}$ = 7.1

Hz, 2H, CH_2CH$_3$), 6.12 (s, 2H, aryl-H), 6.75 (d, J_{H-H} = 16.2 Hz, 1H, =CH), 8.09 (d, J_{H-H} = 16.2 Hz, 1H, =CH).

Ethyl (2*E*,4*Z*)-4-(Ethoxycarbonyl)-5-(2,4,6-trimethoxyphenyl)-2,4-pentadienoate (29):[27] ^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.66 (t, J_{H-H} = 7.2 Hz, 3H, CH$_2$CH_3), δ 0.90 (t, J_{H-H} = 7.2 Hz, 3H, CH$_2$CH_3).

Ethyl 3-Bis(2,4,6-trimethoxyphenyl)propionate (30): ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.21 (t, J_{H-H} = 7.2 Hz, 3H, CH$_2$CH_3), 3.06 (d, 2H, J_{H-H} = 8.6 Hz, CH$_2$) 3.68 (s, 6H, OCH$_3$), 3.75 (s, 12H, OCH$_3$), 5.17 (t, 1H, J_{H-H} = 8.5 Hz, CH), 6.06 (s, 4H, aryl-H).

Ethyl (*Z*)-3-(2,5-Dimethoxyphenyl)propenoate (32):[27] ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.21 (t, J_{H-H} = 7.1 Hz, 3H, CH$_2$CH_3), 3.76 (s, 3H, COH$_3$), 4.28 (q, J_{H-H} = 7.2 Hz, 2H, CH_2CH$_3$), 5.99 (d, J_{H-H} = 12.4 Hz, 1H, =CH), 6.81 (d, J_{H-H} = 9.0 Hz, 1H, aryl-H), 6.87 (dd, J_{H-H} = 3.0 Hz, J_{H-H} = 9.0 Hz, 1H, aryl-H), 7.14 (d, J_{H-H} = 12.4 Hz, 1H, =CH), 7.22 (d, J_{H-H} = 3.0 Hz, 1H, aryl-H).

Ethyl (*Z*)-3-(2,5-Dimethoxyphenyl)propenoate (33):[27] ^{1}H NMR (CDCl$_3$, 300 MHz): δ 6.52 (d, J_{H-H} = 16.0 Hz, 1H, =CH), 7.98 (d, J_{H-H} = 16.0 Hz, 1H, =CH).

Ethyl 3-Bis(2,5-Dimethoxyphenyl)propionate (34):[27] ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.23 (t, J_{H-H} = 6.9 Hz, 3H, CH$_2$CH_3), 3.01 (d, 2H, J_{H-H} = 8.0 Hz, CH$_2$) 3.73 (s, 6H, OCH$_3$), 4.16 (q, J_{H-H} = 7.0 Hz, 4H, CH_2CH$_3$), 5.15 (t, J_{H-H} = 8.4 Hz, 1H, CH), 6.65-6.80 (m, 6H, aryl-H).

Ethyl (*Z*)-3-(1-Naphthyl)propenoate (36): ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.05 (t, J_{H-H} = 7.1 Hz, 3H, CH$_2$CH_3), 4.04 (q, J_{H-H} = 7.1 Hz, 2H, CH_2CH$_3$), 6.28 (d, J_{H-H} = 12.0 Hz, 1H, =CH), 7.48-7.56 (m, 4H, naphthyl-H), 7.59 (d, J_{H-H} = 12.0 Hz, 1H, =CH), 7.85-7.95 (m, naphthyl-H).

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20. The structures of the alkene side products **6** and **7** shown in eq 6 where suggested by the GCMS software. Due to the low abundance, the matching quality of MS-spectra is relatively poor, therefore other isomeric structures cannot be ruled out. It is suggested, that in the actual structures the methoxy groups are located at the C–C double bond, and these two side products might likely be *E* and *Z* isomers which would be more plausible, cf. also ref. 3.

21. Similar to the statement in footnote 20 above, the structures in eq 9 are suggested by the GC-MS software, where stereo- and regiochemistry is not considered.

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27. For this compound not all ^{1}H NMR signals could be observed or assigned unambiguously due to overlap with other signals or low intensity.

Table 1. Selected bond lengths (Å) and angles (°) of [Au(dppbO)Cl] (**1**).

Au–Cl	2.2812(15)	P2–O	1.488(4)
Au–P1	2.2310(15)	C1–C2	1.411(8)
P1–C1	1.835(6)	C2–C3	1.388(8)
P1–C7	1.826(6)	C3–C4	1.384(8)
P1–C13	1.815(6)	C4–C5	1.374(8)
P2–C2	1.828(6)	C5–C6	1.385(8)
P2–C19	1.804(6)	C1–C6	1.402(8)
P2–C25	1.813(6)		
P1–Au–Cl	179.04(6)		
C1–P1–Au	115.33(19)		
C2–C1–P1	123.6(4)		
C1–C2–P2	122.7(4)		
O–P2–C2	112.8(3)		

Table 2. Intramolecular short contacts in [Au(dppbO)Cl] (**1**).

Contact	Length	Length - v.d. Waals bond length
Au···O	3.057(4)	-0.123
P1···O	2.939(4)	-0.381

C13···O	2.890(7)	-0.330

Table 3 Hydration of alkynes[a]

Entry	Alkyne	mol% [Au]	mol% $AgBF_4$	mol% HBF_4	*t* (h)	*T* (°C)	Yield %[b]
1[c]	phenylacetylene	10	10	20	120	28	>95
2	phenylacetylene	10	10	20	23	80	>95
3	phenylacetylene	10	0	0	23	25	3
4	phenylacetylene	0	10	0	23	25	0
5	phenylacetylene	0	0	20	23	25	0
6	phenylacetylene	10	10	20	23	28	20
7	diphenylacetylene	10	10	20	23	28	13
8	1-hexyne	10	10	20	23	28	>99
9	2-hexyne	10	10	20	23	28	>99
10[d]	phenylacetylene	1	1	2	23	25	<5
11[e]	phenylacetylene	1	1	2	23	25	42

[a]Standard conditions: 0.2 mL of H_2O, 1.4 mL of MeOH, 0.3 mmol of alkyne, 0.03 mmol of complex **1**, 0.03 mmol of $AgBF_4$; [b]by GCMS using n-octane standard; [c]0.2 mL of H_2O, 0.4 mL of MeOH, 1.5 mL of CH_2Cl_2; [d]2 mL of H_2O, 14 mL of MeOH, 3 mmol of alkyne, 0.03 mmol of complex **1**, 0.03 mmol of $AgBF_4$; [e]16 mL of MeOH, 3 mmol of alkyne, 0.03 mmol, of complex **1**, 0.03 mmol of $AgBF_4$.

Table 4 Hydrarylation of ethylpropiolate (cf. eq 11 and Chart 1)[a]

Entry	Arene	*t* (min)	Conv. %[b]	Products (yield %)[b]
1[c]	pentamethylbenzene (**18**)	10	96	**19** (96), **20** (traces)
2[d]	pentamethylbenzene (**18**)	1440	0	
3[a]	pentamethylbenzene (**18**)	50	99	**19** (99), **20** (traces)
4[a]	mesitylene (**21**)	30	>99	**22** (73), **23** (13), **25** (traces)
5[e]	mesitylene (**21**)	50	90	**22** (22), **23** (14), **24** (13), **25** (1)
6[a]	1,3,5-trimethoxybenzene (**26**)	60	96	**27** (10), **28** (40), **29** (17), **30** (18), other (11)
7[a]	1,4-dimethoxybenzene (**31**)	80	87	**32** (34), **33** (traces), **34** (47), other (6)
8[a]	naphthalene (**35**)	95	60	**36** (52), other (8)

[a]Standard conditions: 0.1 mol% of complex **1**, 0.1 mol% of $AgBF_4$, 10 mol% of HBF_4, 1 mL of CH_2Cl_2, 10 mmol of ethylpropiolate **17**, 10 mmol of arene, T = 25 °C; [b]conversion of ethylpropiolate **17** or arene and product yield determined by ^1H NMR spectroscopy; [c]10 mmol (1 equiv) of HBF_4; [d]no HBF_4 added; [e]5 mmol of mesitylene **21**, 10 mmol of ethylpropiolate **17**.

Table 5. Crystal data and structure refinement for [Au(dppbO)Cl] **1**.

Empirical formula	$C_{30}H_{24}AuClOP_2$	
Formula weight	694.85	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.8665(14) Å	α = 90°.
	b = 30.022(5) Å	β = 96.811(2)°.
	c = 9.8878(16) Å	γ = 90°.
Volume	2613.4(7) Å^3	
Z	4	
Density (calculated)	1.766 g/cm^3	
Absorption coefficient	5.876 mm^{-1}	
F(000)	1352	
Crystal size	0.32 × 0.17 × 0.13 mm^3	
Theta range for data collection	2.18-27.00°.	
Index ranges	h, ±11; k, ±38; l, ±12	
Reflections collected	29185	
Independent reflections/ R_{int}	5702/ 0.0678	
Completeness % to θ	99.8/ 27.00°	
Absorption correction	Semi-empirical from equivalents	
Max/ min transmission	0.4660/ 0.2381	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	5702 / 0 / 316
Goodness-of-fit on F^2	1.029
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0348$, w$R_2 = 0.0677$
R indices (all data)	$R_1 = 0.0691$, w$R_2 = 0.0808$
Max/ min $\Delta\rho$	0.953/ −1.047 e.Å^{-3}