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Synthesis, reactivity and catalytic activity of Au-PAd$_3$ complexes†

Vladislav A. Voloshkin, [a] Marina Saab,[a] Kristof Van Hecke, [a] Sii Hong Lau, [b] Bradley P. Carrow [b] and Steven P. Nolan *[a]

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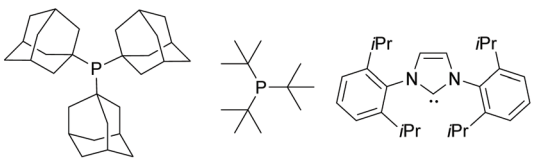
Tri(1-adamantyl)phosphine (PAd$_3$) possesses unique steric and electronic properties positioning it at the border between tertiary phosphines and N-heterocyclic carbenes (NHC). Novel Au-PAd$_3$ complexes were synthesized from the known [Au(PAd$_3$)Cl]. We have optimised reaction conditions for the synthesis of this useful synthon in order to circumvent the formation of the [Au(PAd$_3$)$_2$]Cl. [Au(PAd$_3$)Cl] was used to access a number of derivatives and some were deployed as catalysts. The hydration of alkynes was targeted to gauge the reactivity of Au-PAd$_3$ complexes and permit comparison with NHC and tertiary phosphine congeners.

Introduction

Historically, the initial ligands used in the 'gold rush' of the beginning of the 21st century were tertiary phosphines, followed by extensive use of NHC ligands.[1] The unique large steric and highly electron donating nature of the NHCs (NHCs are more electron donating than electron rich trialkylphoshines)[2] has led to improved complex stability and high catalytic activity achieved *via* enabling intermediacy of LAu$^+$ species.[3]

Recently Carrow and co-workers have reported the straightforward synthesis and unusual properties of tri(1-adamantyl) phosphine (PAd$_3$).[4] The Tolman electronic parameter (TEP) value of 2052.1 cm^{-1} for this ligand is the lowest among known monodentate phosphines. This value is very close to that of the very commonly employed 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr)[5] that has a TEP value of 2051.5 cm^{-1}.[6] PAd$_3$ while being electronically akin to IPr, is less bulky (with a %V_{bur} of 40.5 *vs.* 46.9 for IPr and 40.0 for P^{t}Bu$_3$). These steric and electronic property values place PAd$_3$ at the border between phosphorus and NHC ligands (Scheme 1).

In terms of effectiveness as a catalyst modifier, the PAd$_3$ ligand has already been successfully implemented in Pd-catalysed Suzuki–Miyaura coupling involving deactivated arylboronic acids[7] and in the enantiodivergent C–C bond formation,[8] α-arylation of indolin-3-ones[9] and has shown high catalytic activity for Ni-catalysed ultrahigh-molecular-weight polyethylene synthesis.[10] With the advent of these important reports, it is interesting to note that the use of PAd$_3$ in gold(I) mediated catalysis is at a very early stage and remains almost unexplored to date.



	PAd$_3$	P^{t}Bu$_3$	IPr
TEP, cm^{-1}	2052.1	2056.1	2051.5
%V$_{bur}$	40.5	40.0	46.9

Scheme 1 Comparison of electronic and steric parameters of ligands. The values for %V_{bur} were calculated using SambVca 2.1[11] on the examples of X-ray structures for [Au(L)Cl] complexes.

Only a limited number of Au-PAd$_3$ complexes have been reported to date: [Au(PAd$_3$)Cl] (**1**) by Carrow *et al.*,[4] [Au(PAd$_3$)(NTf$_2$)] and [Au(PAd$_3$)(FSI)] (where NTf$_2$ = bistriflimide, N(SO$_2$CF$_3$)$_2$; FSI = bis(fluorosulfonyl)imide, N(SO$_2$F)$_2$) by Yu *et al.*[12] Only **1** has been implemented as a pre-catalyst for indolizine synthesis, showing better results when compared with P^{t}Bu$_3$, XPhos and SPhos as supporting ligands.[13] This system does however require the use of silver additive, which has been shown to act not simply as an innocent halide abstractor in a number of gold-mediated reactions.[14] High catalyst loadings are also noted as undesirable operating procedures for this transformation and method.

[a]*Department of Chemistry and Center for Sustainable Chemistry, Ghent University, Krijgslaan 281 (S-3), 9000 Ghent, Belgium. E-mail: steven.nolan@ugent.be*
[b]*Department of Chemistry, Princeton University Princeton, NJ 08544, USA*

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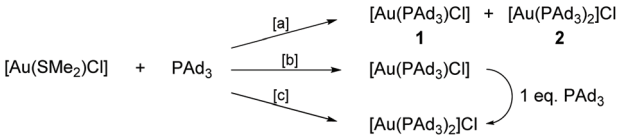
Results and discussion

Synthesis of [Au(PAd$_3$)Cl]

We began our studies with the synthesis of a key synthon leading to Au-PAd$_3$ complexes, namely, the simple [Au(PAd$_3$)Cl] (**1**) reported by Carrow.[4] Using the initial reported procedure, we faced unexpected appearance of additional resonance in the ^{31}P NMR spectrum of the reaction crude. It should be stated that this procedure has been implemented in reports devoted to PAd$_3$ gold complexes but reactions have usually been carried out on a small-scale.

Unexpectedly, scaling up the reaction led to two compounds instead of the expected **1**, as a sole product. Two closely spaced resonances in the ^{31}P NMR spectrum at 81 and 83 ppm, as well as two distinct sets of adamantyl proton resonances showed similar environment near phosphorus atoms in two different complexes. One set of resonances was unambiguously assigned to **1** (81 ppm in ^{31}P NMR), and the second complex was determined to be the bis-phosphine complex [Au(PAd$_3$)$_2$]Cl (**2**). Such complexes are known for a few phosphines, such as PPh$_3$ and PCy$_3$,[15,16] but it was unexpected in the PAd$_3$ reaction as only 1 equivalent of the ligand was employed. While performing NMR characterisation studies, we noticed that only **1** proved soluble in C$_6$D$_6$. This permitted the simple separation and isolation of the two complexes. Furthermore, the addition of 1 equivalent PAd$_3$ to a solution containing **1** in DCM led to the complete conversion of **1** into **2** confirming our assumption about the composition of **2** (Scheme 2).

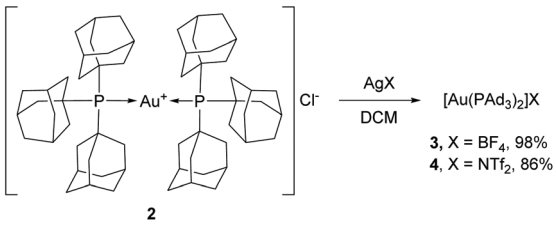


Scheme 2 Variation in reaction product distribution as a function of conditions. Conditions: [a] Simple mixing [Au(DMS)Cl] with PAd$_3$ 1 : 1 in DCM. [b] Slow dropwise addition of PAd$_3$ solution into conc. solution of [Au(DMS)Cl] in DCM. [c] Simple mixing [Au(DMS)Cl] with PAd$_3$ 1 : 2 in DCM.

Since a large amount of undesirable benzene was required for the isolation of **1**, we turned our attention to other methods to generate **1** in high yield. We reasoned that in view of the bulkiness of the ligand, its slow addition to a solution of [Au(DMS)Cl] might prove beneficial. Gratifyingly, this procedure led to the decrease formation of **2**. Ultimately, slow dropwise addition of a PAd$_3$ solution into a concentrated solution of [Au(DMS)Cl] led to exclusive formation of **1**.[17] This slow addition procedure leads to analytically pure material (see ESI† for details).

Reactivity of bis-ligated Au-PAd$_3$ complexes

Counterion in bisphosphine complexes known in gold chemistry can be inner-sphere such as in [Au(PPh$_3$)$_2$Cl][15] or outer-sphere like in [Au(PCy$_3$)$_2$]Cl[16] and [Au(P^{t}Bu$_3$)$_2$]Cl.[18] Because of the steric similarity between P^{t}Bu$_3$ and PAd$_3$, the chloride in **2** should reside outer-sphere. Numerous attempts to determine atom position and connectivity using single X-ray diffraction on single crystal were thwarted in view of significant disorder. A counterion exchange reaction to the much bulkier BF$_4$ and NTf$_2$ counterions was successfully performed to isolate **3** and **4** (Scheme 3). Fortunately, single crystals of **4**, grown from dichloromethane solution by slow vapour diffusion with pentane, permitted successful X-ray diffraction.



Scheme 3 Counterion exchange in [Au(PAd$_3$)$_2$]Cl (**2**).

Comparison of bond angles and lengths values with known [Au(P^{t}Bu$_3$)$_2$]NTf$_2$ did not reveal any significant differences. Linear coordination of gold shown for that compound is slightly distorted in **4**, but the gold metal center is still almost completely surrounded by ligands with the counterion residing in the outer-sphere (Fig. 1).[19]

Based on these results, we conclude that directly mixing the metal source and the ligand in a reaction solvent is undesirable in the case of PAd$_3$ gold catalysis. Formation of undesirable [Au(PAd$_3$)$_2$]X species will likely lead to formation of inactive species. Moreover, we discovered that formation of **2** is irreversible under reaction conditions even in the presence of [Au(DMS)Cl] excess.[20]

Reactivity of mono-ligated Au-PAd$_3$ complexes

Having pure **1** in hand, we initiated study of its reactivity (Scheme 4). Most gold pre-catalysts are used in the presence of additive, which allows for the formation of cationic LAu$^+$

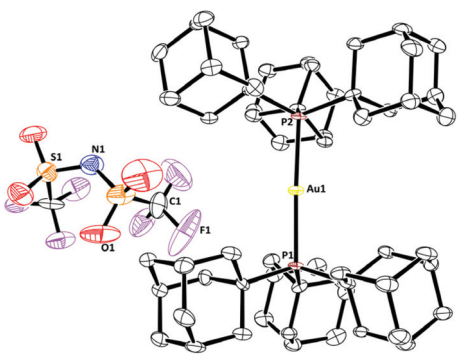
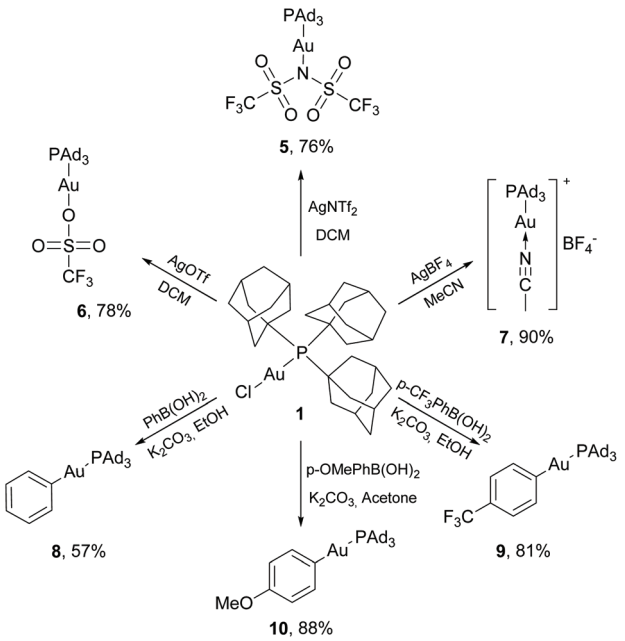


Fig. 1 ORTEP of [Au(PAd$_3$)$_2$]NTf$_2$ (**4**). Solvent molecules and hydrogen atoms are omitted for clarity; thermal ellipsoids are shown with 50% probability level. Selected bond distances (Å) and angles (°): Au(1)–P(1) 2.332, Au(1)–P(2) 2.334, P(1)–Au(1)–P(2) 177.7(1).



Scheme 4 Reactivity of [Au(PAd$_3$)Cl] (**1**).

species *in situ*.[21] Oftentimes silver salts of trifluoromethylsulfonic acid or bis(trifluoromethanesulfonyl)amine are used as additives, to generate [Au(L)X] (X = OTf, NTf$_2$) *in situ*. Complexes [Au(PAd$_3$)NTf$_2$] (**5**) and [Au(PAd$_3$)OTf] (**6**) can be obtained using this classical route in good yields (Scheme 4). X-Ray quality crystals of [Au(PAd$_3$)OTf] (**6**) were grown from dichloromethane solution by slow vapour diffusion with pentane.[19] Metrical parameters for **6** are very similar to those found in [Au(P(*o*-tolyl)$_3$)OTf] (Fig. 2).[22]

Recent developments in alkyne hydroalkoxylation using cationic [Au(NHC)(CH$_3$CN)]BF$_4$ at very low 0.02 mol% catalyst loading[23] prompted our interest in the synthesis of the PAd$_3$ analogue. Stirring of **1** with equimolar amount of AgBF$_4$ in acetonitrile at room temperature afforded **7** in 90% yield.

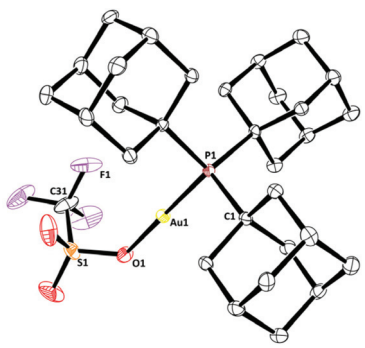


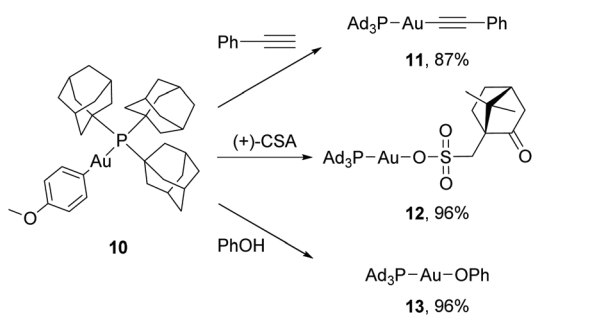
Fig. 2 ORTEP of [Au(PAd$_3$)OTf] (**6**). Two distinct structures exist in the unit cell. Hydrogen atoms are omitted for clarity; thermal ellipsoids are shown with 50% probability level. Selected bond distances (Å) and angles (°): Au(1)–P(1) 2.229, Au(1)–O(1) 2.105, O(1)–S(1) 1.476, P(1)–C(1) 1.893, P(1)–Au(1)–O(1) 177.7(6), Au(1)–O(1)–S(1) 118.6(8), C(1)–P(1)–Au(1) 107.8(7), O(1)–S(1)–C(31) 102.2(2).

Complex **7** was found to be relatively stable in the solid-state but decomposed over 24 hours in air in CDCl$_3$.

In order to circumvent the use of silver reagents to generate cationic gold(I) species, we envisaged adapting a recent procedure we developed to access [Au(PAd$_3$)(aryl)] complexes.[24] The method proves suitable for synthesis of complexes **8**, **9**, **10** using arylboronic acids under very mild conditions. Higher yields were reached with *para*-methoxy and *para*-trifluoromethyl substituents, while phenylboronic acid reacted less effectively. We presume that reaction efficiency is related to solubility properties of reactants in ethanol. Changing the solvent to acetone and increasing of temperature to 60 °C indeed increased the yield from 72% to 88% but only in the case of the *para*-methoxy complex **10**.

The highly basic gold aryl complexes represent important synthons for further functionalization and reactivity. The anisolyl complex **10** was chosen to study the reactivity of PAd$_3$ gold aryl complexes towards different C–H and O–H acids in view of our recent report on the reactivity of the [Au(IPr)(anisolyl)] analogue.[24] Phenylacetylene reacts with **10** relatively rapidly as 2 h at 80 °C in C$_6$D$_6$ is sufficient to lead to complete conversion of starting material to a sole complex, [Au(PAd$_3$)(CCPh)] **11**. This complex was obtained in 87% yield as a white microcrystalline solid (Scheme 5). Recent developments on catalytic activity of sulfonyl gold complexes in alkyne hydration and alkoxylation[25,26] prompted us to focus not only on the OTf derivative but also on optically active counteranions. The presence of a chiral center in the molecule is promising for the development of enantioselective methodologies of the reactions mentioned above. To exemplify this possibility, we subjected **10** to readily available and inexpensive (1*S*)-(+)-camphorsulphonic acid at ambient temperature. This simple route afforded complex **12** in a 96% yield (Scheme 5).

An unexpected result was achieved when the isolation of a phenoxy complex **13** was attempted. Such complexes bearing a NHC ligand were shown to be unstable in solution even at ambient temperature and very reactive in air.[27] Our intent was to use **13** as an intermediate to access the [Au(PAd$_3$)(OH)] complex. However, synthetic efforts employing water did not lead to the formation of the Au-hydroxide. Compound **13** was stable enough to tolerate filtration through basic Al$_2$O$_3$



Scheme 5 Reactivity of [Au(PAd$_3$)(anisolyl)] **10**.

without any decomposition. Such species are quite relevant to catalysis as a gold phenoxide was shown to be an active catalytic species involved in the hydrophenoxylation of alkynes.[28]

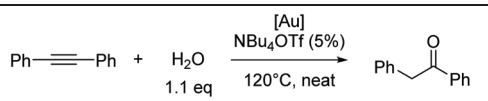
Catalytic studies

In order to begin to map the catalytic landscape of well-defined PAd_3 gold complexes, we selected the hydration of alkynes as a reference reaction using the single component $[Au(PAd_3)NTf_2]$ (**5**) and $[Au(PAd_3)OTf]$ (**6**) catalysts. Similar triflate complex of gold bearing 1,3-bis[2,6-(di-isopropyl)phenyl] imidazol-2-ylidene (IPr) as a ligand was shown to exhibit excellent efficacy under solvent- and acid-free conditions in recent work of Zuccaccia.[29]

Under these conditions Au-PAd_3 complexes proved unsuitable for the hydration of 3-hexyne as were most phosphine complexes examined by Zuccaccia (see Table S1†). Surprisingly, the hydration of diphenylacetylene, known as a more challenging substrate proved efficient (Table 1). Although higher catalyst loading (entries 3 and 5) were needed to reach conversions obtained with [Au(IPr)OTf]. For more robust comparison of catalytic activity of phosphine-coordinated gold we synthesized [Au(JohnPhos)OTf], which has not been tested by Zuccaccia in diphenylacetylene hydration. We performed catalytic reaction under the same conditions with 0.2 mol% loading of [Au(JohnPhos)OTf] (entry 6). Although it also exhibited high performance, **5** and **6** both exhibit slightly superior catalytic performance. To the best of our knowledge, these results are the highest achieved in diphenylacetylene hydration with phosphine-gold catalytic system.

In order to detect possible off-cycle $[Au(PAd_3)_2]^+$ species we also recorded the ^{31}P NMR spectra of reaction samples. None of them indicated formation of phosphine di-coordinated gold, the only resonance observed was attributed to the [Au(PAd_3)X] complex used as catalyst.

Table 1 Gold-catalysed hydration of diphenylacetylene[a,c]



Entry	Catalyst	mol% of the catalyst	Conv. % (time)[b]
1	$[Au(PAd_3)OTf]$	0.05	29 (15 h)
2	$[Au(PAd_3)OTf]$	0.1	62 (4 h) 78 (8 h)
3	$[Au(PAd_3)OTf]$	0.2	90 (4 h) 96 (8 h)
4	$[Au(PAd_3)NTf_2]$	0.1	80 (4 h) 91 (8 h)
5	$[Au(PAd_3)NTf_2]$	0.2	94 (4 h) 96 (8 h)
6	[Au(JohnPhos)OTf]	0.2	86 (4 h) 91 (8 h)

[a] Conditions: Diphenylacetylene (1.75 mmol, 312 mg), NBu_4OTf (0.087 mmol, 34.3 mg) and H_2O (1.92 mmol, 35 μL). [b] Conversion was determined using ^1H NMR and is average of two runs. [c] Control experiments were performed showing 0% conv. after 8 h.

Conclusions

We have reported the synthesis of novel Au-PAd_3 complexes and highlight their stability. An optimized synthetic procedure was devised to obtain $[Au(PAd_3)Cl]$ selectively, circumventing the formation of the $[Au(PAd_3)_2]Cl$ side-product. The reactivity of **1** and of the Au-aryl complexes (**8–10**) were also investigated. Catalytic reactions permit a comparison with the activity of cationic gold complexes **5** and **6** with well-defined analogues and tested for the first time [Au(JohnPhos)OTf]. Comparable results with previously reported [Au(IPr)OTf] catalyst were obtained in the hydration of diphenylacetylene.

Further studies of this family of complexes will be focused on catalytic activity comparison with well-defined NHC analogues that have shown high activity in π-systems functionalisation such as hydroamination and hydroalkoxylation of alkynes.

Experimental

General considerations

All reactions were performed under air, unless otherwise specified. Solvents and reagents were used as received without any further purification. PAd_3 was purchased from Strem and used as received. ^1H, ^{13}C, ^{31}P and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300, 400 or 500 MHz spectrometers at 298 K. Chemical shifts (ppm) in ^1H and ^{13}C are referenced to the residual solvent peak ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CD_2Cl_2: δ_H = 5.32 ppm, δ_C = 54.00 ppm). Coupling constants (*J*) are given in hertz. Abbreviations used in the designation of the signals: s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, dd = doublet of doublets, m = multiplet, q = quadruplet, br q = broad quadruplet. Elemental analyses were performed at London Metropolitan University and Namur University ASBL.

Synthesis of complexes

$[Au(PAd_3)Cl]$ (1)

Procedure A. In a glovebox, a Schlenk vial was charged with [Au(DMS)Cl] (0.30 mmol, 88 mg) and 2 mL of CH_2Cl_2 (DCM). PAd_3 (1.05 eq., 0.315 mmol, 138 mg) was dissolved in 10 mL DCM and added to the [Au(DMS)Cl] solution in one portion. The vial was sealed with a screw cap, taken outside the glovebox and stirred for 30 minutes at room temperature. After this time, removal in vacuum of 2/3 of the DCM from the reaction mixture was followed with addition of 10 mL of EtOH to precipitate the product. The precipitate was collected on a sintered funnel and washed with 10 mL of pentane to afford a white solid. The ^{31}P spectrum contained two singlets, which later were attributed to $[Au(PAd_3)Cl]$ and $[Au(PAd_3)_2]Cl$ complexes.

Procedure B. In a glovebox, [Au(DMS)Cl] (0.75 mmol, 221 mg) was dissolved in a round-bottom flask in 10 mL of DCM. PAd_3 (1.03 eq., 0.77 mmol, 336 mg) was dissolved in 45 mL DCM and transferred to a dropping funnel. While the [Au(DMS)Cl]

solution was efficiently stirred, a solution of PAd_3 was added dropwise (1 drop per second). The clear solution of the resulting product was taken outside the glovebox where 2/3 of the solvent was evaporated in vaccuum and 20 mL of EtOH was added to precipitate the product. The precipitate was collected on a sintered funnel and washed with 10 mL of pentane to afford a white solid (405 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.40 (br s, 18H, CH_2CP), 2.03 (br s, 9H, CH), 1.74 (br q, $^2J_{H-H}$ = 12.4 Hz, 18H, CH_2). ^{31}P NMR (400 MHz, $CDCl_3$): δ 80.85. Elemental analysis calcd (%) for $C_{30}H_{45}AuClP$: C 53.85, H 6.78; found: C 54.03, H 6.81. Analytical data are in agreement with literature values.[4]

[Au(PAd$_3$)$_2$]Cl (2). In a glovebox, [Au(DMS)Cl] (0.1 mmol, 30 mg) and PAd_3 (0.2 mmol, 87 mg) were charged into a reaction vial followed by addition of 5 mL DCM. After 15 minutes of stirring (using magnetic stirring bar), a clear solution was obtained. The solvent was evaporated under reduced pressure to afford a white solid (109 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (br s, 36H, CH_2CP), 2.14 (br s, 18H, CH), 1.79 (br q, $^2J_{H-H}$ = 12.8 Hz, 36H, CH_2). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 48.8 (t, $^1J_{C-P}$ = 6.0 Hz, **C**P), 43.8 (br s, **C**H_2CP), 36.8 (**C**H_2), 29.7 (t, $^3J_{C-P}$ = 4.2 Hz, **C**H). ^{31}P NMR (162 MHz, CD_2Cl_2) δ 82.9. HRMS (ESI-TOF): calcd for $C_{60}H_{90}AuP_2^+$ [M − Cl]$^+$:1069.6178; found: 1069.6138.

[Au(PAd$_3$)$_2$]BF$_4$ (3). [Au(PAd$_3$)$_2$]Cl (0.049 mmol, 54 mg) and $AgBF_4$ (1.05 eq., 0.053 mmol, 10.3 mg) along with a magnetic stirring bar were charged into a scintillation vial, followed by addition of 1 mL DCM. After 30 minutes of stirring, the suspension was filtered through Celite, precipitation with 10 mL of pentane followed by collection on a frit afforded the product as a white solid (60 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (br s, 18H, CH_2CP), 2.14 (br s, 9H, CH), 1.79 (q, $^2J_{H-H}$ = 12.5 Hz, 18H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 48.4 (t, $^1J_{C-P}$ = 6.0 Hz, **C**P), 43.4 (br s, **C**H_2CP), 36.4 (**C**H_2), 29.1 (t, $^3J_{C-P}$ = 4.1 Hz, **C**H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 83.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ −155.1 (F_3B**F**-Au interaction), −155.1. Elemental analysis calcd for $C_{60}H_{90}AuBF_4P_2$: C 62.28, H 7.84; found: C 62.17, H 7.65.

[Au(PAd$_3$)$_2$]NTf$_2$ (4). In a scintillation vial containing a magnetic stir bar, [Au(PAd$_3$)$_2$]Cl (0.039 mmol, 43 mg) was added to a solution of $AgNTf_2$ (1.1 eq., 0.043 mmol, 17 mg) in 4 mL of DCM. In the vial (wrapped in aluminum foil to avoid light) the reaction was stirred at room temperature for 1 h, and then filtered through Celite. Precipitation by addition of 10 mL of pentane to the filtrate followed by collection on a sintered frit, afforded the product as a white solid (45 mg, 86%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 2.48 (br s, 36H, CH_2CP), 2.12 (br s, 18H, CH), 1.80 (br s, 36H, CH_2).^{13}C NMR (75 MHz, CD_2Cl_2) δ 120.5 (q, $^1J_{C-F}$ = 321.6 Hz, CF_3), 48.8 (t, $^1J_{C-P}$ = 6.0 Hz, **C**P), 43.8 (br s, **C**H_2CP), 36.8 (**C**H_2), 29.7 (t, $^3J_{C-P}$ = 4.2 Hz, **C**H).^{31}P NMR (121 MHz, CD_2Cl_2) δ 83.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ −78.7. Elemental analysis calcd (%) for $C_{62}H_{90}AuF_6NO_4P_2S_2$: C 55.14, H 6.72, N 1.04; found: C 55.23, H 6.85, N 0.99.

[Au(PAd$_3$)(NTf$_2$)] (5). In a scintillation vial, [Au(PAd$_3$)Cl] (0.14 mmol, 95 mg) was added to a solution of $AgNTf_2$ (0.14 mmol, 54 mg) in 5.5 mL of DCM. The suspension was magnetically stirred at room temperature for 1 h, and then filtered through Celite. Addition of 10 mL of pentane afforded the product as a white solid (98 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 18H, CH_2CP), 2.07 (s, 9H, CH), 1.76 (q, $^2J_{H-H}$ = 12.4 Hz, 18H, CH_2). ^{31}P NMR (162 MHz, $CDCl_3$) δ 81.1. ^{19}F NMR (471 MHz, $CDCl_3$) δ −75.8. Elemental analysis calcd (%) for $C_{32}H_{45}AuF_6NO_4PS_2$: C 42.06, H 4.96, N 1.53; found: C 42.35, H 4.99, N 1.28. NMR data match previously reported values.[12]

[Au(PAd$_3$)OTf] (6). [Au(PAd$_3$)Cl] (0.075 mmol, 50 mg) and AgOTf (1.05 eq., 0.079 mmol, 20 mg) were charged into a scintillation vial followed by addition of 1.5 mL degassed DCM. The solution was stirred for 30 minutes at room temperature and filtered through Celite. The solvent was evaporated under reduced pressure to afford the product as a white solid (45 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (br s, 18H, CH_2CP), 2.07 (br s, 9H, CH), 1.76 (m, 18H, CH_2).^{13}C NMR (101 MHz, CD_3OD–$CDCl_3$) δ 120.9 (q, $^1J_{C-F}$ = 318.9 Hz, **C**F_3), 48.2 (d, $^1J_{C-P}$ = 17.4 Hz, **C**P), 43.8 (br s, **C**H_2CP), 36.6 (**C**H_2), 29.5 (d, $^3J_{C-P}$ = 8.6 Hz, **C**H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 81.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ −76.79. Elemental analysis calcd (%) for $C_{31}H_{45}AuF_3O_3PS$: C 47.57, H 5.80; found: C 47.69, H 6.05.

[Au(PAd$_3$)(MeCN)]BF$_4$ (7). [Au(PAd$_3$)Cl] (0.075 mmol, 50 mg) and $AgBF_4$ (1.05 eq., 0.079 mmol, 15 mg) were charged into a scintillation vial followed by addition of 1.5 mL degassed MeCN. The solution was magnetically stirred for 30 minutes at room temperature and filtered through Celite. The solvent was evaporated under reduced pressure to afford the product as a white solid (51 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (s, 3H, CH_3), 2.38 (br s, 18H, CH_2CP), 2.09 (br s, 9H, CH), 1.78 (q, $^2J_{H-H}$ = 12.2 Hz, 18H, CH_2).^{13}C NMR (101 MHz, $CDCl_3$) δ 120.5 (**C**N) 47.8 (d, $^1J_{C-P}$ = 16.9 Hz, **C**P), 43.2 (br s, **C**H_2CP), 36.3 (**C**H_2), 29.1 (d, $^3J_{C-P}$ = 8.1 Hz, **C**H), 2.76 (**C**H_3). ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.30. ^{19}F NMR (471 MHz, $CDCl_3$) δ −153.2 (F_3B**F**-Au interaction), −153.2. HRMS (ESI-TOF): calcd for $C_{32}H_{48}AuNP^+$ [M − BF_4]$^+$: 674.3184;found: 674.3155.

[Au(PAd$_3$)Ph] (8). [Au(PAd$_3$)Cl] (0.07 mmol, 45 mg), phenylboronic acid (1.2 eq., 0.08 mmol, 10 mg) and K_2CO_3 (3 eq., 0.21 mmol, 28 mg) were charged into a scintillation vial, followed by addition of 1 mL of EtOH. The suspension was magnetically stirred at 40 °C for 16 h and the solvent was removed under reduced pressure. Addition of 5 mL of benzene permitted filtration through Celite, evaporation of the solvent afforded the product as a white solid (27 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.53 (m, 2H, 2,6-C**H**^{Ph}), 7.30–7.23 (m, 2H, 3,5-C**H**^{Ph}), 7.08–7.01 (m, 1H, 4-C**H**^{Ph}), 2.49 (br s, 18H, CH_2CP), 2.04 (br s, 9H, CH), 1.77 (m, 18H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.47 (d, $^2J_{C-P}$ = 103.7 Hz, **C**^{Ph}Au), 139.5 (2,6-**C**H^{Ph}), 127.65 (d, $^4J_{C-P}$ = 5.2 Hz, 3,5-**C**H^{Ph}), 125.4 (4-**C**H^{Ph}), 46.3 (d, $^1J_{C-P}$ = 10.1 Hz, **C**P), 42.9 (br s, **C**H_2CP), 36.8 (**C**H_2), 29.3 (d, $^3J_{C-P}$ = 8.1 Hz, **C**H). ^{31}P NMR (162 MHz, $CDCl_3$) Issues with combustion of this compound as well as mass spectrometry fragmentation have not permitted us to establish purity by these two methods.

[Au(PAd$_3$)(*p*-CF$_3$Ph)] (9). [Au(PAd$_3$)Cl] (0.07 mmol, 45 mg), (4-(trifluoromethyl)phenyl)boronic acid (1.2 eq., 0.08 mmol,

15 mg) and K_2CO_3 (3 eq., 0.21 mmol, 28 mg) were charged into a scintillation vial along with a magnetic stir bar, followed by addition of 1 mL of EtOH. The suspension was stirred at 40 °C for 16 h and the solvent was evaporated under reduced pressure. Addition of 5 mL of benzene permitted filtration through Celite, evaporation of the solvent afforded the product as a white solid (42 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.63 (m, 2H, 2,6-C**H**^{Ph}), 7.48 (d, ^2J = 7.5 Hz, 2H, 3,5-C**H**^{Ph}), 2.49 (br s, 18H, CH_2CP), 2.06 (br s, 9H, CH), 1.89–1.68 (m, 18H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.6 (d, $^2J_{C-P}$ = 103.4 Hz, **C**–Au), 139.4 (2,6-**C**H^{Ph}), 127.0 (q, $^2J_{C-F}$ = 31.4 Hz, **C**^{Ph}CF_3), 125.1 (q, $^1J_{C-F}$ = 271.5 Hz, **C**F_3), 123.6 (m, 3,5-**C**H^{Ph}), 46.4 (d, $^1J_{C-P}$ = 10.6 Hz, **C**P), 43.0 (br s, **C**H_2CP), 36.7 (**C**H_2), 29.2 (d, ^3J = 8.3 Hz, **C**H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 79.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ −62.3. Elemental analysis calcd for $C_{37}H_{49}AuF_3P$: C 57.07, H 6.34; found: C 57.14, H 6.48.

[Au(PAd$_3$)(*p*-OMePh)] (10). [Au(PAd$_3$)Cl] (0.075 mmol, 50 mg), (4-methoxyphenyl)boronic acid (1.2 eq., 0.09 mmol, 14 mg), K_2CO_3 (3 eq., 0.225 mmol, 31 mg) and a sir bar were charged into a scintillation vial, followed by addition of 1 mL of acetone. The suspension was stirred at 60 °C for 16 h and the solvent was evaporated under reduced pressure. Addition of 5 mL of benzene permitted filtration through Celite, evaporation of the solvent afforded the product as a white solid (49 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.48 (m, 2H, 2,6-C**H**^{Ph}), 6.89 (dd, $^{2,3}J_{H-H}$ = 8.3, 1.0 Hz, 2H, 3,5-C**H**^{Ph}), 3.78 (s, 1H, CH_3O), 2.49 (br s, 18H, CH_2CP), 2.04 (br s, 9H, CH), 1.77 (m, 18H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9 (d, $^2J_{C-P}$ = 105.3 Hz, **C**–Au), 157.6 (**C**^{Ph}O), 139.8 (2,6-**C**H^{Ph}), 113.5 (d, $^4J_{C-P}$ = 5.7 Hz, 3,5-**C**H^{Ph}), 55.3 (**C**H_3O), 46.3 (d, $^1J_{C-P}$ = 10.2 Hz, **C**P), 42.9 (br s, **C**H_2CP), 36.8 (**C**H_2), 29.2 (d, $^3J_{C-P}$ = 8.0 Hz, **C**H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 79.6. Elemental analysis calcd (%) for $C_{37}H_{52}AuOP$: C 59.99, H 7.08; found: C 59.93, H 7.22.

[Au(PAd$_3$)(CCPh)] (11). [Au(PAd$_3$)(*p*-OMePh)] (**10**) (0.08 mmol, 60 mg) along with a stir bar were charged into a scintillation vial, followed by addition of 1 mL of C_6H_6 and phenylacetylene (1.1 eq., 0.09 mmol, 9.8 μL). The suspension was stirred at 80 °C for 2 h and volatiles were evaporated under reduced pressure to afford a white solid (51 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.49 (m, 2H, 2,6-C**H**^{Ph}), 7.24–7.13 (m, 3H, 3,4,5-C**H**^{Ph}), 2.44 (br s, 18H, CH_2CP), 2.03 (br s, 9H, CH), 1.75 (m, 18H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5 (d, $^2J_{C-P}$ = 122.7 Hz, **C**–Au), 132.5 (2,6-**C**^{Ph}H), 127.9 (3,5-**C**^{Ph}H), 126.5 (4-**C**^{Ph}H), 125.5 (d, $^4J_{C-P}$ = 2.5 Hz, 1-**C**^{Ph}), 103.0 (d, $^3J_{C-P}$ = 22.2 Hz, **C**CAu), 46.7 (d, $^1J_{C-P}$ = 14.1 Hz, **C**P), 42.9 (br s, **C**H_2CP), 36.6 (**C**H_2CP), 29.2 (d, $^3J_{C-P}$ = 8.3 Hz, **C**H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 78.9. Elemental analysis calcd (%) for $C_{38}H_{50}AuP$: C 62.12, H 6.86; found: C 61.95, H 6.63.

[Au(PAd$_3$(CSA)] (12). [Au(PAd$_3$)(*p*-OMePh)] (**10**) (0.068 mmol, 50 mg), (1*S*)-(+)-10-camphorsulfonic acid (1.02 eq., 0.069 mmol, 16 mg) and a stir bar were charged into a scintillation vial, followed by addition of 1 mL of $CHCl_3$. The suspension was stirred at room temperature for 16 h and then the solvent was evaporated under reduced pressure. Addition of 5 ml of DCM to the solid residue permitted a filtration through Celite, evaporation of the solvent and trituration with 10 mL of pentane followed by filtration afforded the product as a white solid (56 mg, 96%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.60 (d, $^1J_{H-H}$ = 15.0 Hz, 1H, C**H**HS), 2.99 (d, $^1J_{H-H}$ = 15.0 Hz, 1H, CH**H**S), 2.87–2.69 (m, 1H, CH^{CSA}), 2.57–2.24 (m, 20H), 2.04 (s, 11H), 1.89 (d, $^2J_{H-H}$ = 18.2 Hz, 1H), 1.83–1.57 (m, 20H), 1.47–1.30 (m, 1H), 1.17 (s, 3H, CH_3), 0.87 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.0 (**C**=O), 58.6 (**C**CH_2S), 48.0 (**C**H_2S), 47.3 (d, $^1J_{C-P}$ = 18.1 Hz, **C**P), 42.9 (br s, **C**H_2CP), 42.9 (**C**^{CSA}H_2), 36.4 (**C**^{CSA}H_2), 29.1 (d, $^3J_{C-P}$ = 8.6 Hz, **C**^{Ad}H), 27.2 (**C**^{CSA}H_2), 25.0 (**C**^{CSA}H), 20.4 (**C**H_3), 20.0 (**C**H_3). ^{31}P NMR (162 MHz, $CDCl_3$) δ 79.3. Elemental analysis calcd (%) for $C_{40}H_{60}AuO_4PS$: C 55.55, H 6.99; found: C 55.33, H 6.86.

[Au(PAd$_3$)(OPh)] (13). [Au(PAd$_3$)(*p*-OMePh)] (**10**) (0.07 mmol, 50 mg), phenol (0.07 mmol, 6.7 mg) and a stir bar were charged into a scintillation vial, followed by addition of 1 mL of C_6H_6. The suspension was stirred at 60 °C for 2 h and the solvent was evaporated under reduced pressure to afford a white solid (47 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.11 (m, 2H, 3,5-C**H**^{Ph}), 7.05–6.98 (m, 2H, 2,6-C**H**^{Ph}), 6.65–6.58 (m, 1H, 3-C**H**^{Ph}), 2.44 (br s, 18H, CH_2CP), 2.04 (br s, 9H, CH), 1.75 (m, 18H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8 (**C**^{Ph}O), 129.8 (3,5-**C**^{Ph}H), 118.6 (d, J = 1.6 Hz, 2,6-**C**^{Ph}H), 115.6 (4-**C**^{Ph}H), 46.8 (d, $^1J_{C-P}$ = 17.9 Hz, **C**P), 42.9 (br s, **C**H_2CP), 36.5 (**C**H_2), 29.1 (d, $^3J_{C-P}$ = 8.6 Hz, **C**H). ^{31}P NMR (162 MHz, $CDCl_3$) δ 74.5. Elemental analysis calcd (%) for $C_{36}H_{50}AuOP$: C 59.50, H 6.94; found: C 59.13, H 6.56.

[Au(JohnPhos)Cl] (14). In a glovebox [Au(DMS)Cl] (0.36 mmol, 100 mg) and JohnPhos (1 eq., 0.36 mmol, 104 mg) was mixed in a scintillation vial. 2 mL of DCM was added and vial was taken out the glovebox. Reaction mixture was stirred for 4 h at room temperature. After that solvent was evaporated under reduced pressure and solid was dissolved in minimum amount of DCM and precipitated with 10 mL of pentane. Precipitate was filtered on a sintered funnel and washed with 10 mL of pentane to afford a white solid (174 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90–7.82 (m, 1H, CH_{Ar}), 7.62–7.53 (m, 1H, CH_{Ar}), 7.53–7.46 (m, 2H, CH_{Ar}), 7.46–7.39 (m, 2H, CH_{Ar}), 7.34–7.28 (m, 1H, CH_{Ar}), 7.15–7.10 (m, 2H, CH_{Ar}), 1.44 (s, 9H, CH_3), 1.38 (s, 9H, CH_3). ^{31}P NMR (121 MHz, $CDCl_3$) δ 59.94.

[Au(JohnPhos)OTf] (15). [Au(JohnPhos)Cl] (0.19 mmol, 100 mg) and AgOTf (1.05 eq., 0.20 mmol, 51 mg) was mixed in a dark in a scintillation vial covered with foil. 2 mL of DCM was added reaction mixture was stirred for 4 h at room temperature. After that reaction mixture was filtered through celite using 5 mL of DCM. Filtrate was evaporated under reduced pressure to afford white solid (107 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82–7.89 (m, 1H, CH_{Ar}), 7.61–7.51 (m, 3H, CH_{Ar}), 7.51–7.43 (m, 2H, CH_{Ar}), 7.39–7.33 (m, 1H, CH_{Ar}), 7.18–7.11 (m, 2H, CH_{Ar}), 1.43 (s, 9H, CH_3), 1.38 (s, 9H, CH_3). ^{31}P NMR (121 MHz, $CDCl_3$) δ 57.21 (br s). NMR shifts of the product corresponded the reported values.[30]

Catalytic tests

Hydration of 3-hexyne. [Au(PAd$_3$)X], 3-hexyne (199 μL, 1.75 mmol), H_2O (34.6 μL, 1.925 mmol) and NBu_4OTf (34.3 mg,

0.0875 mmol) were mixed in a 2 mL glass screw-top vial. The reaction mixture was stirred (rpm 1500) at 30 °C. The progress of the reaction was monitored by ^{1}H NMR. The conversion was calculated from the integral intensities of the –CH_2– protons.

Hydration of diphenylacetylene. [Au(PAd_3)X], diphenylacetylene (312 mg, 1.75 mmol), H_2O (34.6 mL, 1.925 mmol) and NBu_4OTf (34.3 mg, 0.0875 mmol) were mixed in a 4 mL glass screw-top vial. Reaction mixture was stirred (rpm 1500) at 120 °C. The progress of the reaction was monitored by ^{1}H NMR. The conversion was calculated from the integral intensities of suitable aromatic protons. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05–7.98 (m, 2H, CH_{Ar}), 7.60–7.52 (m, 1H, CH_{Ar}), 7.50–7.42 (m, 2H, CH_{Ar}), 7.38–7.21 (m, 5H, CH_{Ar}), 4.29 (s, 2H, C*H*CO). NMR shifts of the product corresponded the reported values.[26]

Conflicts of interest

There are no conflicts to declare.

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