



Catalytic ring-closing reactions of gold compounds containing bis(phosphino)ferrocene ligands

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ABSTRACT

The efficiency of various gold compounds containing bis(phosphino)ferrocene ligands for catalyzing ring-closing reactions was examined. Six commercially available bis(phosphino)ferrocene ligands: 1,1'-bis(di-*tert*-butylphosphino)ferrocene (dtbpf), 1,1'-bis(diphenylphosphino)ferrocene (dppf), 1,1'-bis(dicyclohexylphosphino)ferrocene (dcpf), 1,1'-bis(diiso-propylphosphino)ferrocene (dippf), 1-diphenylphosphino-1'-di-*tert*-butylphosphinoferrocene (dppdtbpf) and 1,1'-bis(5-methyl-2-furanylphosphino)ferrocene (dfurpf) were employed in this study. In addition to the previously reported $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ (PP = dtbpf, dppf, dcpf, dippf or dppdtbpf) compounds, $[\text{Au}_2\text{Cl}_2(\mu\text{-dfurpf})]$ was synthesized and characterized by NMR spectroscopy, cyclic voltammetry and X-ray crystallography. All of these gold compounds react with $\text{Na}[\text{BArF}_4]$ ($\text{BArF}_4 = \text{tetrakis}(3,5\text{-bis}(\text{trifluoromethyl})\text{phenyl})\text{borate}$) to remove a chloride and yield the cationic monochlorides, $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-PP})]^+$. The effectiveness of the $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ and $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-PP})][\text{BArF}_4]$, either pre-formed or generated *in situ*, compounds for the catalytic intramolecular alkyne hydroalkoxylation of (Z)-3-methylpent-2-en-4-yn-1-ol was examined in CDCl_3 and toluene- d_8 . The ring-closing of *N*-(prop-2-yn-1-yl)benzamide was also examined and was efficiently carried out in toluene- d_8 using $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-PP})][\text{BArF}_4]$ (PP = dtbpf, dppf, dcpf, dippf, dppdtbpf or dfurpf). In addition, $[\text{Au}_2\text{Cl}_2(\mu\text{-dppe})]$ and $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-dppe})][\text{BArF}_4]$ were examined as catalysts for these ring-closing reactions in order to determine if the ferrocene backbone of the bis(phosphino)ferrocene ligands was important for catalysis.

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1. Introduction

Bis(phosphino)ferrocene ligands are frequently employed in a variety of catalytic reactions [1–4]. Among this class of ligands, 1,1'-bis(diphenylphosphino)ferrocene (dppf) has been the most studied. Although a majority of those studies have focused on palladium compounds, dppf-containing compounds are known for nearly all of the transition metals [5,6]. The first reported gold compound of dppf was $[\text{Au}_2\text{Cl}_2(\mu\text{-dppf})]$; this report included NMR as well as ^{57}Fe and ^{197}Au Mössbauer data for this compound in addition to the X-ray crystal structure [7]. There have been several additional reports of the crystal structure of this compound as well [8–12]. A variety

of reactions of $[\text{Au}_2\text{Cl}_2(\mu\text{-dppf})]$ have been examined, the majority of which have involved replacing the chlorides with ligands such as metal clusters [13–24], organic groups [25–29], ER groups (E = S, Se, N) [12,29–48], halides [12], phosphines [29,49,50] and sulfides [51]. In addition, there have been a variety of studies of the biological activity of various thio- and seleno-derivatives of $[\text{Au}_2\text{Cl}_2(\mu\text{-dppf})]$ for their anti-malaria, anti-cancer and anti-microbial properties [52–56].

Aside from dppf, various bis(phosphino)ferrocene ligands with hydrocarbon substituents are known (Table 1). These include 1,1'-bis(di-*tert*-butylphosphino)ferrocene (dtbpf), 1,1'-bis(diiso-propylphosphino)ferrocene (dippf), 1,1'-bis(dicyclohexylphosphino)ferrocene (dcpf), 1-(diphenylphosphino)-1'-(di-*tert*-butylphosphino)ferrocene (dppdtbpf) and 1,1'-bis(5-methyl-2-furanylphosphino)ferrocene (dfurpf). With the exception of dfurpf, the $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ compounds for these ligands have been synthesized and the electrochemistry has been examined [57–60]. In addition, the X-ray crystal structures of $[\text{Au}_2\text{Cl}_2(\mu\text{-dippf})]$ [11] and $[\text{Au}_2\text{Cl}_2(\mu\text{-dtbpf})]$ [61]

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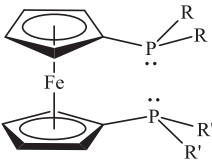
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Table 1
1,1'-bis(phosphino)ferrocene ligands.

	R	R'	Ligand
	Ph	Ph	dppf
	ⁱ Pr	ⁱ Pr	dippf
	Cy	Cy	dcpf
	^t Bu	^t Bu	dtbpf
	Ph	^t Bu	dppdtbpf
	5-methyl-2-furanyl	5-methyl-2-furanyl	dfurpf

have been reported. There are two reports of reactions of $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ compounds in which the bis(phosphino)ferrocene ligand is not dppf. The reaction of dippf with $\text{Na}[\text{AuCl}_4]$ in the presence of NaBr results in the formation of $[\text{Au}_2\text{Br}_2(\mu\text{-dippf})]$ in which the halide exchange could presumably happen before or after dippf coordination [11]. Recently, it was found that a chloride ligand could be removed from the $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ (PP = dppf, dtbpf or dppdtbpf) compounds using $[\text{N}(p\text{-C}_6\text{H}_4\text{Br})_3][\text{BARF}_{20}]$ (BARF_{20} = tetrakis(pentafluorophenyl)borate) yielding a cationic species with a bridging chloride, $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-PP})][\text{BARF}_{20}]$ [61].

Surprisingly, very little catalytic work [62–69] has been done with any of these $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ compounds. Although no actual catalysis was performed, a thorough NMR study revealed that upon exchanging the chloride ligands in $[\text{Au}_2\text{Cl}_2(\mu\text{-dppf})]$ with triflate, the resulting species reacts with triphenylphosphine to yield a compound in which one of the gold atoms has been abstracted [70]. In the conversion of phenylacetylene to fluoromethylphenyl ketone, $[\text{Au}_2\text{Cl}_2(\mu\text{-dppf})]$ was among the poorest catalysts studied [71]. While not catalytic, $[\text{Au}_2\text{Cl}_2(\mu\text{-dppf})]$ was converted *in situ* to $[\text{Au}_2(\text{OTf})_2(\mu\text{-dppf})]$ which was employed in the stoichiometric ring-closing of an alkynol [72]. Finally, the combination of AuI and dppf was found to be a highly efficient catalyst in the Sonogashira reaction of terminal alkynes with aryl iodides and bromides [73].

While the catalytic applications of $[\text{Au}_2\text{Cl}_2(\mu\text{-bis(phosphino)ferrocene})]$ compounds are limited, the activity of similar compounds suggests that there are potential applications for these compounds. The catalytic intramolecular alkyne hydroalkoxylation of (Z)-3-methylpent-2-en-4-yn-1-ol was examined using 1'-(diphenylphosphino)-1-cyanoferrocene gold chloride $[(\text{C}_5\text{H}_4\text{CN})\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2\text{AuCl})]$ as the catalyst [74]. Intramolecular alkyne hydroalkoxylation was accomplished in 65% conversion when $[(\text{C}_5\text{H}_4\text{CN})\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2\text{AuCl})]$ was used as the catalyst and rose to >97% when the chloride ligand of $[(\text{C}_5\text{H}_4\text{CN})\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2\text{AuCl})]$ was abstracted with a silver salt.

Transposition of the carbon and nitrogen atoms to give 1'-(diphenylphosphino)-1-isocyanoferrocene gold chloride $[(\text{C}_5\text{H}_4\text{NC})\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2\text{AuCl})]$ dramatically alters the catalytic properties of the compound [75]. No catalytic activity is displayed for the intramolecular alkyne hydroalkoxylation of (Z)-3-methylpent-2-en-4-yn-1-ol by $[(\text{C}_5\text{H}_4\text{NC})\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2\text{AuCl})]$. However, upon adding a second equivalent of gold chloride to give $[(\text{C}_5\text{H}_4\text{NCAuCl})\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2\text{AuCl})]$ the catalytic intramolecular alkyne hydroalkoxylation conversion increases to 89%. The chloride free dication dimer, $[\text{Au}_2(\mu\text{-}(\text{C}_5\text{H}_4\text{NC})\text{Fe}(\text{C}_5\text{H}_4\text{PPh}_2))_2]^{2+}$, does not catalyze this intramolecular alkyne hydroalkoxylation reaction. In a related study, the removal of a chloride makes a significant difference in the catalytic activity. In the catalytic ring-closing of 4-methyl-N-[(5-methyl-2-furanyl)methyl]-N-2-propyn-1-yl-benzenesulfonamide, $[(\text{Ph}_3\text{PAu})_2(\mu\text{-Cl})][\text{BF}_4]$ was found to be a more efficient catalyst than $[\text{Ph}_3\text{PAu}][\text{BF}_4]$ generated *in situ* by the reaction of $[\text{PPh}_3\text{AuCl}]$ with $\text{Ag}[\text{BF}_4]$ [76]. While $[\text{PPh}_3\text{Au}]^+$ is proposed to be the active catalyst in both cases, reforming $[(\text{Ph}_3\text{PAu})_2(\mu\text{-Cl})][\text{BF}_4]$

provides a potential resting state which is proposed to limit catalyst decomposition. This previous work suggests that $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-PP})]^+$ compounds may be potent catalysts in ring-closing reactions. Work by Katz suggests that short gold-gold distances constitute a potentially stabilizing metal-metal interaction [77]. The short gold-gold interaction found in $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-dtbpf})]^+$ may stabilize these compounds [61], providing an ideal resting state for catalysts in intramolecular alkyne hydroalkoxylation reactions. Herein the catalytic activity of several $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ and $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-PP})]^+$ compounds containing bis(phosphino)ferrocene ligands in the intramolecular alkyne hydroalkoxylation of (Z)-3-methylpent-2-en-4-yn-1-ol and N-(prop-2-yn-1-yl)benzamide is reported. In addition, the synthesis of $[\text{Au}_2\text{Cl}_2(\mu\text{-dfurpf})]$ was carried out and the catalytic activity of this compound and $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-dfurpf})]^+$ was examined in the aforementioned intramolecular alkyne hydroalkoxylation reactions.

2. Results and discussion

The compound $[\text{Au}_2\text{Cl}_2(\mu\text{-dfurpf})]$ was synthesized following a procedure similar to that employed for other $[\text{Au}_2\text{Cl}_2(\mu\text{-bis(phosphino)ferrocene})]$ compounds. The compound was characterized by ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and the assignment of the proton and carbon signals was accomplished using COSY, DEPT, HMBC and HSQC experiments. The oxidative electrochemistry of $[\text{Au}_2\text{Cl}_2(\mu\text{-dfurpf})]$ was examined in CH_2Cl_2 and a single reversible oxidation was observed (Fig. 1). Oxidation of the free dfurpf under similar conditions gave a chemically reversible wave. The 5-methyl-2-furanyl substituents of dfurpf have been noted to make the phosphorus atoms poorly sigma donating in comparison to the phosphorus atoms in dppf [78–80]. With respect to the iron center in these compounds, the oxidation of the iron in both free dfurpf and $[\text{Au}_2\text{Cl}_2(\mu\text{-dfurpf})]$ occurs at potentials less positive than that of the dppf analogues (Table 2) indicating that the iron is more electron rich in the dfurpf compounds.

The X-ray crystal structure of $[\text{Au}_2\text{Cl}_2(\mu\text{-dfurpf})]$ was determined (Fig. 2). The structure is similar to related gold compounds with bis(phosphino)ferrocene ligands. The geometry of the gold atoms is linear and the planes defined by the C_5 rings are approximately parallel. The steric bulk of the dfurpf ligand was calculated using percent buried volume ($\%V_{\text{bur}}$) [81] and compared to other bis(phosphino)ferrocene ligands in gold compounds (Table 3). The $\%V_{\text{bur}}$ calculations suggest that for these gold compounds the dfurpf ligand is significantly bulkier (3.7% greater) than dppf but slightly less bulky than dippf (1.1% less). This is opposite what was calculated for the closely related $[\text{Au}_2\text{Cl}_2(\mu\text{-}((1\text{-PPh}_2\text{-3-}^t\text{Bu-C}_5\text{H}_3)_2\text{Fe}))]$ and $[\text{Au}_2\text{Cl}_2(\mu\text{-}((1\text{-P(fur)}_2\text{-3-}^t\text{Bu-C}_5\text{H}_3)_2\text{Fe}))]$ compounds in which the phenyl ligand was found to have a $\%V_{\text{bur}}$ 2.4% greater than that of the furanyl ligand [82]. Similarly, dppf was calculated to have a $\%V_{\text{bur}}$ 1.5% greater than dfurpf in $[\text{MCl}_2(\text{PP})]$ ($\text{M} = \text{Pd}$ or Pt) complexes [83]. A plausible explanation for this discrepancy can be found in the τ angle which is the torsion angle $\text{C}_A\text{-X}_A\text{-X}_B\text{-C}_B$ in which C

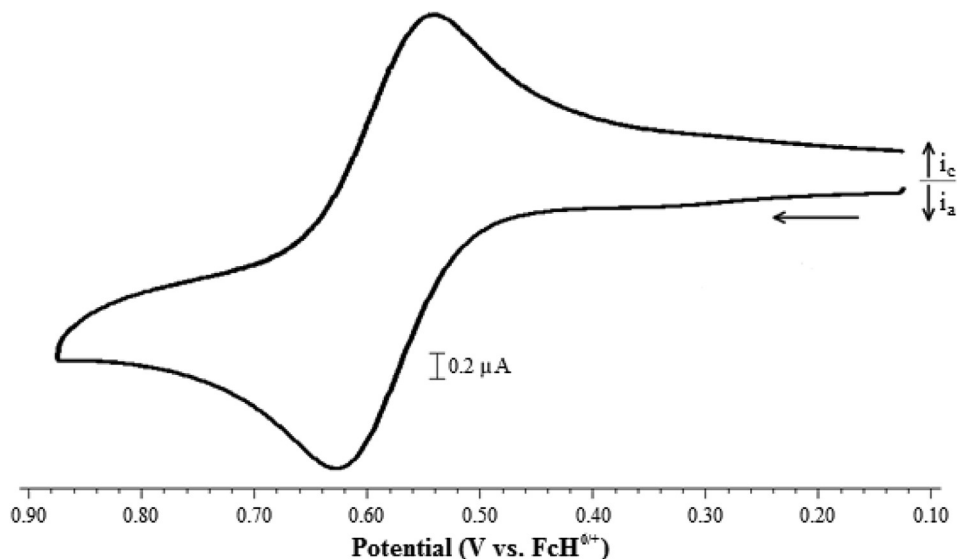


Fig. 1. CV scan of 1.0 mM $[\text{Au}_2\text{Cl}_2(\mu\text{-dfurpf})]$ in CH_2Cl_2 with 0.1 M $[\text{NBu}_4][\text{PF}_6]$ as the supporting electrolyte measured at 100 mV s^{-1} .

Table 2

CV data (E in V vs. $\text{FcH}^{0/+}$) for ligands and $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ compounds in CH_2Cl_2 .

	Free ligand	$[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$	Reference
dppf	0.23 ^a	0.64	[60]
dippf	0.05 ^a	0.54	[59]
dcpf	0.02 ^a	0.52	[57]
dtbpf	0.06	0.56	[58]
dppdtbpf	0.11 ^a	0.59	[60]
dfurpf	0.15 ^a	0.58	This work

^a Chemically reversible waves.

represents the carbon atom of the C_5 ring bonded to phosphorus and X represents the centroid of the C_5 ring. The substituents in $[\text{Au}_2\text{Cl}_2(\mu\text{-dfurpf})]$ adopt a gauche eclipsed arrangement ($\tau \sim 72^\circ$) whereas in dppf the substituents adopt an antiperiplanar arrangement ($\tau \sim 180^\circ$) [5]. The relative proximity of the phosphine groups in the solid state structure of $[\text{Au}_2\text{Cl}_2(\mu\text{-dfurpf})]$ may account for this difference. There is also an intramolecular aurophilic interaction [84,85] between the gold centers in $[\text{Au}_2\text{Cl}_2(\mu\text{-dfurpf})]$. With the exception of $[\text{Au}_2\text{Cl}_2(\mu\text{-(C}_5\text{H}_4\text{P(OC}_{10}\text{H}_6)_2(\mu\text{-S))}_2\text{Fe})]$, all of the other reported structures of $[\text{Au}_2\text{Cl}_2(\text{bis}(\text{phosphino})\text{ferrocene})]$ structures, exhibit intermolecular gold-gold distances well outside the range to be considered aurophilic interactions. The addition of the *tert*-butyl groups in the 3-position of the C_5 rings in $[\text{Au}_2\text{Cl}_2(\mu\text{-(1-PPh}_2\text{-3-}^t\text{Bu-C}_5\text{H}_3)_2\text{Fe})]$ and $[\text{Au}_2\text{Cl}_2(\mu\text{-(1-P(fur)}_2\text{-3-}^t\text{Bu-C}_5\text{H}_3)_2\text{Fe})]$ appears to increase the favorability of the aurophilic interaction as these compounds both display an intramolecular aurophilic interaction. It is unclear why $[\text{Au}_2\text{Cl}_2(\mu\text{-dfurpf})]$

The $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-PP})][\text{BARF}_{20}]$ compounds were previously prepared by the reaction of $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ (PP = dppf, dppdtbpf or dtbpf) with $[\text{N}(p\text{-C}_6\text{H}_4\text{Br})_3][\text{BARF}_{20}]$ [61]. A more straightforward route to synthesize the related $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-PP})][\text{BARF}_{24}]$ compounds was developed by reacting $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ with one equivalent of $\text{Na}[\text{BARF}_{24}]$. These compounds were characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR. In general, there is a small (~ 2 ppm) downfield shift of the signal(s) in the ^{31}P NMR spectrum upon removal of the chloride ligand from these compounds. The notable exception being $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-dfurpf})][\text{BARF}_{24}]$ which exhibits an upfield shift in the ^{31}P NMR spectrum. The NMR data for these compounds is found to be in good agreement with the previously reported data for the $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-PP})][\text{BARF}_{20}]$ ($\mu\text{-PP}$ = dppf, dppdtbpf or dtbpf) compounds [61]. In order to determine if the chloride abstraction was

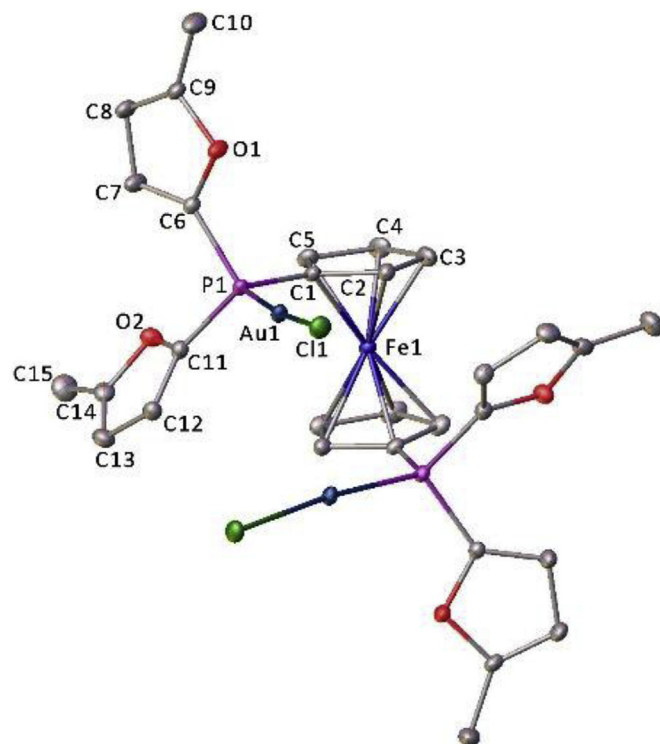


Fig. 2. ORTEP drawing of $[\text{Au}_2\text{Cl}_2(\mu\text{-dfurpf})]$. Thermal ellipsoids are drawn at the 50% probability level and the H atoms were omitted for clarity. Select measurements: $\text{Au}(1)\text{-Cl}(1)$ 2.2792(7) Å, $\text{Au}(1)\text{-P}(1)$ 2.2146(7) Å, $\text{Au}\text{-Au}$ (intramolecular) 3.60240(19) Å, $\text{Au}\text{-Au}$ (intermolecular) 7.2857(2) Å, $\text{P}(1)\text{-Au}(1)\text{-Cl}(1)$ 173.58(2), θ (tilt angle of the C_5 rings) 4.43(17) and $\text{X}_\text{A}\text{-Fe-X}_\text{B}$ 174.93(10).

reversible, 1 molar equivalent of $[\text{PPN}]\text{Cl}$ was added to a solution of $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-dtbpf})][\text{BARF}_{24}]$ which resulted in an immediate conversion back to $[\text{Au}_2\text{Cl}_2(\mu\text{-dtbpf})]$ as indicated by $^{31}\text{P}\{^1\text{H}\}$ NMR.

The gold-catalyzed intramolecular alkyne hydroalkoxylation reaction of (Z)-3-methylpent-2-en-4-yn-1-ol to yield 2,3-dimethylfuran was examined in CDCl_3 (Eq. (1)) [89,90]. When the $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ compounds were used as catalyst precursors, intramolecular alkyne hydroalkoxylation occurred in low yield

Table 3
Percent buried volume (%V_{bur}) and τ angles of [Au₂Cl₂(μ -PP)] compounds.

Compound	%V _{bur}	τ (°) ^a	Au...Au (Å)	Ref.
[Au ₂ Cl ₂ (μ -dfurpf)]	37.7	68.7(3)	3.60240(19) ^b	
[Au ₂ Cl ₂ (μ -dppf)]	34.0	180.0(2)	6.4589(2) ^c	[9]
[Au ₂ Cl ₂ (μ -dippf)]	38.8	142.4(2)	7.2460(5) ^c	[11]
[Au ₂ Cl ₂ (μ -dtbpf)]	41.6	138.28(16)	8.1373(2) ^c	[61]
[Au ₂ Cl ₂ (μ -(C ₅ H ₄ P(NMe ₂) ₂) ₂ Fe)]	38.4	180.0(3)	6.1376(2) ^c	[86]
[Au ₂ Cl ₂ (μ -(C ₅ H ₄ P(NC ₄ H ₄) ₂) ₂ Fe)]	35.2 ^d	179.6(6)	4.4998(5) ^c	[87]
[Au ₂ Cl ₂ (μ -(C ₅ H ₄ P((OC ₁₀ H ₆) ₂ (μ -S)) ₂ Fe)]	46.8	2.4(3)	3.1752(4)	[88]
[Au ₂ Cl ₂ (μ -((1-PPh ₂ -3- ^t Bu-C ₅ H ₃) ₂ Fe)))]	42.4 ^d	79.0(3) ^e	3.0781(6) ^b	[82]
[Au ₂ Cl ₂ (μ -((1-Pfur ₂ -3- ^t Bu-C ₅ H ₃) ₂ Fe)))] ^f	40.0	55.8(7) ^e	3.2349(9) ^b	[82]

^a Torsion angle C_A-X_A-X_B-C_B, with C being the carbon bound to phosphorus and X the centroid of the C₅ ring.^b Nearest intramolecular Au...Au distance.

^d Average of two values.

^e Calculated as part of this work.

^f fur = 5-methyl-2-furanyl.

(Table 4). However, when 1 molar equivalent of Na[BarF₂₄] was added to generate the [Au₂(μ -Cl)(μ -PP)][BarF₂₄] compounds *in situ*, the solution changed color from yellow to yellow-brown upon addition of the (Z)-3-methylpent-2-en-4-yn-1-ol and intramolecular alkyne hydroalkoxylation was detected via ¹H NMR. There appears to be a steric effect of the bis(phosphino)ferrocene ligand on the gold catalyst; as the ligand increases in size, the percent conversion to the furan product decreased. Based on previous studies [76], it is likely that during the catalytic reaction the chloride bridge is broken generating [Au(μ -PP)AuCl]⁺ as the active catalyst. In [Au₂(μ -Cl)(μ -dppdtbpf)]⁺ opening of the chloride bridge could result in the chloride remaining coordinated to either the gold bound to the -PPh₂ group or the gold bound to the -P^tBu₂ group. As the intramolecular alkyne hydroalkoxylation yield is similar to that found for dppf, it seems likely that the bridge opening of [Au₂(μ -Cl)(μ -dppdtbpf)]⁺ occurs so that the chloride remains coordinated to the gold bound to the -P^tBu₂ group.

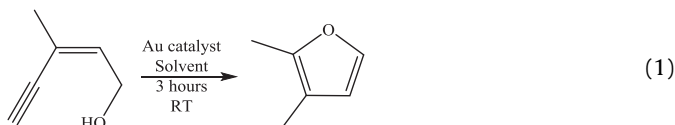


Table 4
Catalyst loading and percent conversion of (Z)-3-methylpent-2-en-4-yn-1-ol to 2,3-dimethylfuran in CDCl₃.

Pre-catalyst	Additive	Mol. Cat.	% Conversion
[Au ₂ Cl ₂ (μ -dppf)]		1.0%	<5%
[Au ₂ Cl ₂ (μ -dippf)]		1.0%	<5%
[Au ₂ Cl ₂ (μ -dcpf)]		1.0%	<5%
[Au ₂ Cl ₂ (μ -dtbpf)]		1.0%	<5%
[Au ₂ Cl ₂ (μ -dppdtbpf)]		1.0%	<5%
[Au ₂ Cl ₂ (μ -dfurpf)]		1.0%	18%
[Au ₂ Cl ₂ (μ -dppe)]		1.0%	36%
[Au ₂ Cl ₂ (μ -dppf)]	Na[BarF ₂₄]	1.0%	Quantitative
[Au ₂ Cl ₂ (μ -dippf)]	Na[BarF ₂₄]	1.0%	92%
[Au ₂ Cl ₂ (μ -dcpf)]	Na[BarF ₂₄]	1.0%	73%
[Au ₂ Cl ₂ (μ -dtbpf)]	Na[BarF ₂₄]	1.0%	8%
[Au ₂ Cl ₂ (μ -dppdtbpf)]	Na[BarF ₂₄]	1.0%	84%
[Au ₂ Cl ₂ (μ -dfurpf)]	Na[BarF ₂₄]	1.0%	Quantitative
[Au ₂ Cl ₂ (μ -dppe)]	Na[BarF ₂₄]	1.0%	Quantitative
[Au ₂ (μ -Cl)(μ -dtbpf)] ⁺		1.0%	20%
[Au ₂ Cl ₂ (μ -dppf)] ^a	Na[BarF ₂₄]	0.1%	12%
[Au ₂ Cl ₂ (μ -dppf)] ^{a,b}	Na[BarF ₂₄]	0.1%	>95%
[Au ₂ Cl ₂ (μ -dppf)] ^c	Na[BarF ₂₄]	0.1%	54%
[Au ₂ Cl ₂ (μ -dppf)]	Na[PF ₆]	1.0%	36%
[Au ₂ Cl ₂ (μ -dppf)]	Na[BF ₄]	1.0%	<5%
[Au ₂ Cl ₂ (μ -dppf)]	K[BarF ₂₀]	1.0%	Quantitative
No catalyst	Na[BarF ₂₄]	1.0%	0%

^a Reaction performed with ten-fold increase in the amount of solvent and substrate.

^b After 8 days of stirring.

^c Reaction performed with a ten-fold increase in the amount of substrate.

In addition to examining the catalytic activity of the [Au₂(μ -Cl)(μ -PP)][BarF₂₄] compounds generated *in situ*, a catalytic reaction using isolated [Au₂(μ -Cl)(μ -dtbpf)][BarF₂₀] as the catalyst precursor was examined. This method generated the furan product in slightly higher yield (20%) than when the catalyst was generated *in situ* (8%). To examine the effect of adding excess Na[BarF₂₄] to the reaction, two equivalents of Na[BarF₂₄] were added to [Au₂Cl₂(μ -dtbpf)]. However, the catalytic activity of this mixture was not significantly different from that of adding one equivalent of Na[BarF₂₄]. To ensure that the Na[BarF₂₄] was not acting as a catalyst, a reaction was performed without any gold compound present and no product was detected. Finally, [Au₂Cl₂(μ -dppe)] was examined as the catalyst precursor to examine the necessity of the ferrocene backbone in the bisphosphine ligand. The intramolecular alkyne hydroalkoxylation occurred in 36% conversion when [Au₂Cl₂(μ -dppe)] was added to the reaction mixture. Upon performing the reaction in the presence of 1 molar equivalent of Na[BarF₂₄], intramolecular alkyne hydroalkoxylation was quantitative by ¹H NMR.

The most efficient gold catalysts with a bis(phosphino)ferrocene ligand for this intramolecular alkyne hydroalkoxylation reaction were found to contain dppf or dfurpf. From electrochemical data these are among the least electron donating ligands employed in this study. In terms of steric parameters, the previously discussed uncertainty in the %V_{bur} of dfurpf prevents definitive assignment of dppf as the least bulky ligand, and therefore the efficiency of these catalysts could be due to electronic, steric or a combination of both parameters. However, as dppf was found to be among the most efficient and easily obtained, additional studies were performed employing [Au₂Cl₂(μ -dppf)] as the catalyst precursor. The catalytic intramolecular alkyne hydroalkoxylation using [Au₂Cl₂(μ -dppf)] and one molar equivalent of either Na[PF₆] or Na[BF₄] gave significantly lower conversion than when Na[BarF₂₄] was used. This is likely due to the low solubility of either the Na[X] (X = BF₄⁻ or PF₆⁻) salts or the resulting [Au₂(μ -Cl)(μ -dppf)][X] compounds as solids were observed in the reaction mixtures. However, the intramolecular alkyne hydroalkoxylation reaction was quantitative when one equivalent of K[BarF₂₀] was used with [Au₂Cl₂(μ -dppf)]. The choice of the counter ions in gold catalyzed reactions can be quite important to the catalytic efficiency [91,92].

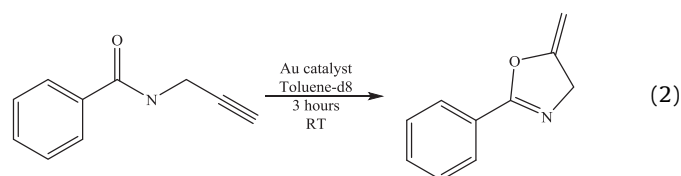
The viability of these gold compounds as catalysts in this intramolecular alkyne hydroalkoxylation reaction was also examined at a lower catalyst loading. The percent mol. catalyst was decreased to 0.1% and two separate reactions using [Au₂(μ -Cl)(μ -dppf)][BarF₂₄] were performed. One solution was prepared by increasing the amounts of CDCl₃, DCE and (Z)-3-methylpent-2-en-4-yn-1-ol tenfold. After stirring for 3 h at RT the ¹H NMR spectra showed 12% conversion to the furan product. The solution was allowed to stir for a total of 8 days and at that point the conversion

was greater than 95%. A second experiment was performed in which only the amount of the (Z)-3-methylpent-2-en-4-yn-1-ol was increased tenfold. After stirring for 3 h at RT there was 54% conversion to the furan product. These results suggest that the catalyst loading can be decreased and still allow for a reasonable amount of intramolecular alkyne hydroalkoxylation.

To examine the effect of solvent, the intramolecular alkyne hydroalkoxylation reaction of (Z)-3-methylpent-2-en-4-yn-1-ol was also performed in toluene- d_8 (Table 5). Similar to the reactions in $CDCl_3$, the $[Au_2Cl_2(\mu-PP)]$ compounds were poor catalysts and the $[Au_2(\mu-Cl)(\mu-PP)][BARF_{24}]$ compounds were much more efficient at intramolecular alkyne hydroalkoxylation. All of the $[Au_2(\mu-Cl)(\mu-PP)][BARF_{24}]$ compounds resulted in quantitative conversion of (Z)-3-methylpent-2-en-4-yn-1-ol to the desired furan product using 1 mol percent catalyst. The catalyst was decreased to 0.1 mol percent by decreasing the amount of $[Au_2(\mu-Cl)(\mu-PP)][BARF_{24}]$ added to the reaction. Under these conditions $[Au_2(\mu-Cl)(\mu-dfurpf)][BARF_{24}]$ was clearly the most efficient catalyst with a ferrocenyl ligand, essentially matching the efficiency of the dppe compound. Further lowering of the catalyst loading was attempted using 0.01 mol percent $[Au_2(\mu-Cl)(\mu-dppf)][BARF_{24}]$, however, no intramolecular alkyne hydroalkoxylation was observed. In addition, $[Au_2(\mu-Cl)(\mu-dppf)][BARF_{24}]$ displayed continued catalytic activity as indicated by the addition of a second aliquot of (Z)-3-methylpent-2-en-4-yn-1-ol after the initial three hours resulting in quantitative conversion to 3,4-dimethylfuran.

As 1.0 mol % of $[Au_2(\mu-Cl)(\mu-dppf)][BARF_{24}]$ was an effective catalysts for the intramolecular alkyne hydroalkoxylation of (Z)-3-methylpent-2-en-4-yn-1-ol, the ability of this compound to catalyze ring-closing reactions in other systems was examined. Using the same conditions as were employed for the intramolecular alkyne hydroalkoxylation of (Z)-3-methylpent-2-en-4-yn-1-ol, reactions of propargyl ether, 5-(trimethylsilyl)4-pentyn-1-ol, 4-pentyn-1-ol, 2-ethynylbenzyl alcohol, allyl phenyl ether and *N*-(prop-2-yn-1-yl)benzamide were examined in toluene- d_8 . Of these reactions, only *N*-(prop-2-yn-1-yl)benzamide gave the desired ring-closing product [93–99], 4,5-dihydro-5-methylene-2-phenyl-oxazole (Eq. (2)). Further ring-closing reactions of *N*-(prop-2-yn-1-yl)benzamide with the other monochloride catalysts ($[Au_2(\mu-Cl)(\mu-PP)][BARF_{24}]$, PP = dpfp, dipfp, dcpf, dfurpf, or dppdtbpf) showed

quantitative ring-closing with the exception of $[Au_2(\mu-Cl)(\mu-dtbpf)][BARF_{24}]$ (Table 6).



In summary, the reaction of $[Au_2Cl_2(\mu-PP)]$ (PP = dpfp, dipfp, dcpf, dtbpf, dppdtbpf or dfurpf) with $Na[BArF_{24}]$ results in formation of the corresponding $[Au_2(\mu-Cl)(\mu-PP)][BARF_{24}]$ species. The efficiency of both the $[Au_2Cl_2(\mu-PP)]$ and the *in situ* generated $[Au_2(\mu-Cl)(\mu-PP)][BARF_{24}]$ compounds in catalyzing the intramolecular alkyne hydroalkoxylation reaction of (Z)-3-methylpent-2-en-4-yn-1-ol was examined. The $[Au_2Cl_2(\mu-PP)]$ compounds did not efficiently catalyze the intramolecular alkyne hydroalkoxylation reaction while the $[Au_2(\mu-Cl)(\mu-PP)][BARF_{24}]$ compounds were able to catalyze the reaction in varying yields in chloroform and quantitatively in toluene- d_8 . For this system it is unclear if the catalyst efficiency is affected by the phosphine ligands in terms of steric, electronic or a combination of both factors. Unlike the $[Au_2Cl_2(\mu-PP)]$ containing bis(phosphino)ferrocene ligands, $[Au_2Cl_2(\mu-dppe)]$ catalyzed the intramolecular alkyne hydroalkoxylation in moderate yield while $[Au_2(\mu-Cl)(\mu-dppe)][BARF_{24}]$ led to quantitative intramolecular alkyne hydroalkoxylation. The catalyst $[Au_2(\mu-Cl)(\mu-dppf)][BARF_{24}]$ was unsuccessful at catalyzing ring-closing for five additional substrates. In addition, several other additives besides $Na[BArF_{24}]$ were examined for *in situ* generation of the catalyst; $K[BArF_{20}]$ was successful while $Na[PF_6]$ and $Na[BF_4]$ were not. The catalyst loading was altered and can be decreased from 1.0% to 0.1% while still yielding high conversion of (Z)-3-methylpent-2-en-4-yn-1-ol to 2,3-dimethylfuran. When the catalyst loading is decreased to 0.01%, the desired furan product was not formed. The efficacy of the *in situ* generated $[Au_2(\mu-Cl)(\mu-PP)]^+$ compounds in catalyzing the ring-closing reaction of *N*-(prop-2-yn-1-yl)benzamide was examined in toluene- d_8 . The $[Au_2(\mu-Cl)(\mu-PP)]^+$ compounds were able to catalyze ring-closing of this system quantitatively with all ligands except dtbpf.

3. Experimental

3.1. General experimental methods

Unless otherwise noted, all reactions were performed under argon by standard Schlenk techniques at 21 ($\pm$ 1) °C. Methanol, chloroform, 1,2-dichloroethane, toluene- d_8 and deuteriochloroform were purchased from Fisher Scientific and used as purchased. The chloroform, 1,2-dichloroethane, toluene- d_8 and deuteriochloroform were stored over molecular sieves. 2,2'-dithioethanol, sodium tetrafluoroborate ($Na[BF_4]$) and sodium hexafluorophosphate (Na

Table 5

Catalyst loading and percent conversion of (Z)-3-methylpent-2-en-4-yn-1-ol to 2,3-dimethylfuran in toluene- d_8 .

Pre-catalyst	Additive	Mol. Cat.	% Conversion
$[Au_2Cl_2(\mu-dppf)]$		1.0%	<5%
$[Au_2Cl_2(\mu-dippf)]$		1.0%	10%
$[Au_2Cl_2(\mu-dcpf)]$		1.0%	24%
$[Au_2Cl_2(\mu-dtbpf)]$		1.0%	0%
$[Au_2Cl_2(\mu-dppdtbpf)]$		1.0%	0%
$[Au_2Cl_2(\mu-dfurpf)]$		1.0%	0%
$[Au_2Cl_2(\mu-dppe)]$		1.0%	0%
$[Au_2Cl_2(\mu-dppf)]$	$Na[BArF_{24}]$	1.0%	Quantitative
$[Au_2Cl_2(\mu-dippf)]$	$Na[BArF_{24}]$	1.0%	Quantitative
$[Au_2Cl_2(\mu-dcpf)]$	$Na[BArF_{24}]$	1.0%	Quantitative
$[Au_2Cl_2(\mu-dtbpf)]$	$Na[BArF_{24}]$	1.0%	Quantitative
$[Au_2Cl_2(\mu-dppdtbpf)]$	$Na[BArF_{24}]$	1.0%	Quantitative
$[Au_2Cl_2(\mu-dfurpf)]$	$Na[BArF_{24}]$	1.0%	Quantitative
$[Au_2Cl_2(\mu-dppe)]$	$Na[BArF_{24}]$	1.0%	Quantitative
$[Au_2Cl_2(\mu-dppf)]$	$Na[BArF_{24}]$	0.1%	10%
$[Au_2Cl_2(\mu-dippf)]$	$Na[BArF_{24}]$	0.1%	18%
$[Au_2Cl_2(\mu-dcpf)]$	$Na[BArF_{24}]$	0.1%	34%
$[Au_2Cl_2(\mu-dtbpf)]$	$Na[BArF_{24}]$	0.1%	20%
$[Au_2Cl_2(\mu-dppdtbpf)]$	$Na[BArF_{24}]$	0.1%	6%
$[Au_2Cl_2(\mu-dfurpf)]$	$Na[BArF_{24}]$	0.1%	53%
$[Au_2Cl_2(\mu-dppe)]$	$Na[BArF_{24}]$	0.1%	54%
No catalyst	$Na[BArF_{24}]$	1.0%	0%

Table 6

Catalyst loading and percent conversion of *N*-(prop-2-yn-1-yl)benzamide to 5-Methylene-2-phenyl-4,5-dihydrooxazole in toluene- d_8 .

Pre-catalyst	Additive	Mol. Cat.	% Conversion
$[Au_2Cl_2(\mu-dppf)]$	$Na[BArF_{24}]$	1.0%	Quantitative
$[Au_2Cl_2(\mu-dippf)]$	$Na[BArF_{24}]$	1.0%	Quantitative
$[Au_2Cl_2(\mu-dcpf)]$	$Na[BArF_{24}]$	1.0%	Quantitative
$[Au_2Cl_2(\mu-dtbpf)]$	$Na[BArF_{24}]$	1.0%	83%
$[Au_2Cl_2(\mu-dppdtbpf)]$	$Na[BArF_{24}]$	1.0%	Quantitative
$[Au_2Cl_2(\mu-dfurpf)]$	$Na[BArF_{24}]$	1.0%	Quantitative
$[Au_2Cl_2(\mu-dppe)]$	$Na[BArF_{24}]$	1.0%	Quantitative
No catalyst	$Na[BArF_{24}]$	1.0%	0%

[PF₆]) were purchased from Aldrich and used without further purification. Purification of CH₂Cl₂ and Et₂O was performed using methods similar to those previously described [100]. Tetrabutylammonium hexafluorophosphate ([NBu₄][PF₆]) was purchased from Aldrich and dried under vacuum at 100 °C prior to use. (Z)-3-Methylpent-2-en-4-yn-1-ol was purchased from Ark Pharm or Arctom Chemicals. Propargyl ether, 5-(trimethylsilyl)4-pentyn-1-ol, 4-pentyn-1-ol, 2-ethynylbenzyl alcohol and allyl phenyl ether were purchased from Aldrich. All bis(phosphino)ferrocene ligands, bis(triphenylphosphine)iminium chloride ([PPN]Cl), H₂AuCl₄·H₂O and [Au₂Cl₂(μ-dppe)] were purchased from Strem Chemical and used without further purification. Potassium tetrakis(pentafluorophenyl)borate (K[BArF₂₀]) was purchased from Alfa Aesar. N-(prop-2-yn-1-yl)benzamide was purchased from Enamine. The gold compounds with bis(phosphino)ferrocene ligands (dppf [7], dippf [59], dcpf [57], dtbpf [58] and dppdtbpf [60]), [Au₂(μ-Cl)(μ-dtbpf)][BArF₂₀] [61] and Na[BArF₂₄] (BArF₂₄ = tetrakis-3,5-bis(trifluoromethyl)phenylborate) was prepared according to literature methods [101]. NMR spectra were obtained in CDCl₃ and toluene-d₈ using a Bruker Avance III HD 400 FT-NMR. The ¹H and ¹³C{¹H} NMR spectra were referenced using internal TMS and the ³¹P{¹H} NMR spectra were referenced using external 85% H₃PO₄. Elemental analysis was performed by Midwest Microlab.

3.2. General synthetic chemical procedures

3.2.1. [Au₂Cl₂(μ-dfurpf)]

A solution of H₂AuCl₄·H₂O (0.1368 g, 0.364 mmol) in a mixture of DI water (1 mL) and methanol (5 mL) was prepared and stirred at 0 °C for 15 min. A solution of 2,2'-dithioethanol (0.164 mL) in methanol (1 mL) was added dropwise to the H₂AuCl₄·H₂O solution and the resulting solution was stirred at 0 °C for 15 min. A solution of the dfurpf ligand (0.1038 g, 0.182 mmol) in a mixture of chloroform (7.5 mL) and methanol (3 mL) was added to the H₂AuCl₄·H₂O solution and the reaction stirred overnight during which time the solution was allowed to slowly warm to room temperature. Methanol (20 mL) was then added to solution. The resulting solution was filtered and the remaining yellow solid was dried in vacuo giving 0.1652 g (88% yield) of the product as a yellow solid. Single crystals of [Au₂Cl₂(μ-dfurpf)] were grown by vapor diffusion of Et₂O into a solution of the compound in CH₂Cl₂. Anal. Calcd for C₃₀H₂₈Au₂Cl₂FeO₄P₂: C, 34.81; H, 2.73. Found: C, 34.66; H, 2.86. ¹H NMR (CDCl₃) δ (ppm): 6.96 (t, J = 3.18 Hz, 4H, furan-C₃H), 6.11 (m, 4H, furan-C₄H), 4.55 (m, 8H, -C₅H₄), 2.39 (s, 12H, -CH₃). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 160.0 (d, J = 5.9 Hz, furan-C₅), 141.5 (d, J = 96.0 Hz, furan-C₂), 125.3 (d, J = 24.8 Hz, furan-C₃), 107.9 (d, J = 9.3 Hz, furan-C₄), 75.1 (d, J = 16.1 Hz, α-C₅H₄), 74.7 (d, J = 10.2 Hz, β-C₅H₄), 69.9 (d, J = 82.9 Hz, ipso-C₅H₄), 14.2 (s, Me). ³¹P{¹H} NMR (CDCl₃) δ (ppm): 15.9 (s).

3.2.2. Characterization of [Au₂(μ-Cl)(PP)][BArF₂₄] compounds

The [Au₂Cl₂(μ-PP)] compounds (~10 mg, 0.10 mmol) and one equivalent of Na[BArF₂₄] were dissolved in ~1 mL CDCl₃.

3.2.2.1. [Au₂(μ-Cl)(dppf)][BArF₂₄]. ¹H NMR δ (ppm). 7.72 (s, 8H, [BArF₂₄]⁻), 7.60–7.48 (m, 24H, [BArF₂₄]⁻ and -C₆H₅), 4.48 (s, 4H, -C₅H₄), 4.40 (s, 4H, -C₅H₄). ³¹P{¹H} NMR δ (ppm): 27.2 (s).

3.2.2.2. [Au₂(μ-Cl)(dippf)][BArF₂₄]. ¹H NMR δ (ppm). 7.70 (s, 8H, [BArF₂₄]⁻), 7.53 (s, 4H), 4.63 (br s, 4H, -C₅H₄), 4.43 (s, 4H, -C₅H₄), 2.33 (m, 4H, -CHMe₂), 1.24 (dd, J = 17.4, 7.0 Hz, 6H, -CH₃), 1.20 (dd, J = 10.7, 7.0 Hz, 6H, -CH₃). ³¹P{¹H} NMR δ (ppm): 52.1 (s).

3.2.2.3. [Au₂(μ-Cl)(dcpf)][BArF₂₄]. ¹H NMR δ (ppm). 7.70 (s, 8H, [BArF₂₄]⁻), 7.52 (s, 4H, [BArF₂₄]⁻), 4.60 (br s, 4H, -C₅H₄), 4.41 (br s,

4H, -C₅H₄), 2.18–1.06 (m, 44H), 2.17–1.52 (m, 24H, -C₆H₁₁), 1.39–1.05 (m, 20H, -C₆H₁₁). ³¹P{¹H} NMR δ (ppm): 43.4 (s).

3.2.2.4. [Au₂(μ-Cl)(dtbpf)][BArF₂₄]. ¹H NMR δ (ppm). 7.75 (s, 8H, [BArF₂₄]⁻), 7.51 (s, 4H, [BArF₂₄]⁻), 4.67 (br s, 4H, -C₅H₄), 4.45 (br s, 4H, -C₅H₄), 1.38 (d, J = 16.1 Hz, 36H, -CH₃). ³¹P{¹H} NMR δ (ppm): 72.0 (s).

3.2.2.5. [Au₂(μ-Cl)(dppdtbpf)][BArF₂₄]. ¹H NMR δ (ppm). 7.72 (s, 8H, [BArF₂₄]⁻), 7.62–7.48 (m, 14H, [BArF₂₄]⁻), and -C₆H₅), 4.87 (br s, 2H, -C₅H₄), 4.62 (br s, 2H, -C₅H₄), 4.48 (m, 2H, -C₅H₄), 4.44 (m, 2H, -C₅H₄), 1.35 (d, J = 15.6 Hz, 18H, -CH₃). ³¹P{¹H} NMR δ (ppm): 72.6 (s, -P^tBu₂), 27.7 (s, -PPh₂).

3.2.2.6. [Au₂(μ-Cl)(dfurpf)][BArF₂₄]. ¹H NMR δ (ppm). 7.70 (s, 8H, [BArF₂₄]⁻), 7.51 (s, 4H, [BArF₂₄]⁻), 6.92 (s, 4H, furanyl), 6.14 (s, 4H, furanyl), 4.61 (s, 4H, -C₅H₄), 4.42 (s, 4H, -C₅H₄), 2.39 (s, 12H, -CH₃). ³¹P{¹H} NMR δ (ppm): 16.4 (s).

3.3. Electrochemistry procedure

All cyclic voltammetry experiments were conducted at room temperature (21 ± 1 °C) using a CH Instruments Model CHI260D potentiostat. Experiments were performed under an argon atmosphere. Experiments were performed with analyte concentrations of 1.0 mM in methylene chloride (10.0 mL) using 0.1 M [NBu₄][PF₆] as the supporting electrolyte. A glassy carbon working electrode (1.0 mm disk) that had been polished with 1.0 μm then 0.25 μm diamond paste and rinsed with methylene chloride prior to use was used as the working electrode. The experiments also employed a platinum wire counter electrode and a nonaqueous Ag/AgCl pseudo-reference electrode that was separated from the solution by a frit. At the end of the experiments Ferrocene was added for use as an internal reference. Data were background subtracted. Experiments were conducted at scan rates of 100–1000 mV s⁻¹ in 100 mV s⁻¹ increments. All data are reported at a scan rate of 100 mV s⁻¹.

3.4. X-ray diffraction studies

All operations were performed on a Bruker-AXS Kappa Apex II CCD diffractometer with 0.71073 Å MoK_α radiation. All diffraction manipulations, including data collection, integration, scaling, and absorption corrections were carried out using the Bruker Apex2 software [102]. Unit cell parameters were obtained from 60 data frames, 0.5° φ, from three different sections of the Ewald sphere. Data collection was carried out at 100K, using a frame time of 5 s and a detector distance of 51 mm. The optimized strategy used for data collection consisted of two phi and six omega scan sets, with 0.5° steps in phi or omega; completeness was 99.9%. A total of 2882 frames were collected. Final cell constants were obtained from the xyz centroids of 9824 reflections after integration.

From the systematic absences, the observed metric constants and intensity statistics, space group C2/c was chosen initially; subsequent solution and refinement confirmed the correctness of this choice. The structure was solved using SIR-92 [103], and refined (full-matrix-least squares) using the Oxford University Crystals for Windows program [104]. The asymmetric unit contains half a molecule of the complex (Z = 4; Z' = 1/2). All non-hydrogen atoms were refined using anisotropic displacement parameters. After location of H atoms on electron-density difference maps, the H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H in the range 0.93–0.98 Å and U_{iso} (H) in the range 1.2–1.5 times U_{eq} of the parent

atom), after which the positions were refined with riding constraints [105]. The final least-squares refinement converged to $R_1 = 0.0209$ ($I > 2\sigma(I)$, 4339 data) and $wR_2 = 0.0464$ (F^2 , 4557 data, 186 parameters).

3.5. Catalytic studies

Unless otherwise specified, the catalytic reactions of each $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ compound were carried out using the following reaction conditions under an atmosphere of argon. A solution was prepared by dissolving 0.01 mmol of $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ in 2.0 mL CDCl_3 or toluene- d_8 and 0.70 mL 1,2-dichloroethane (DCE) which was included as an integration standard. Then 1.0 mmol of (Z)-3-methylpent-2-en-4-yn-1-ol or *N*-(prop-2-yn-1-yl)benzamide was added and the resulting solution was stirred for 3 h at room temperature. A sample of the reaction mixture was transferred to an NMR tube and the $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra were collected. The $[\text{Au}_2(\mu\text{-Cl})(\mu\text{-PP})][\text{BARF}_{24}]$ catalysts were generated *in situ* by adding 1 molar equivalent of $\text{Na}[\text{BARF}_{24}]$ with the desired $[\text{Au}_2\text{Cl}_2(\mu\text{-PP})]$ complex and stirring the solution for approximately 5 min prior to the addition of (Z)-3-methylpent-2-en-4-yn-1-ol or *N*-(prop-2-yn-1-yl)benzamide. Reported yields are the average of three reactions.

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