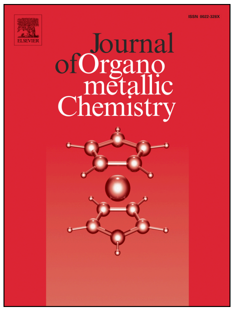

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# Hydroamination reactions catalyzed by $[Au_2(\mu\text{-Cl})(\mu\text{-bis(phosphino)ferrocene})][BArF_{24}]$

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## Abstract

1,1'-bis(phosphino)ferrocene ligands are commonly employed in a variety of catalytic systems. These ligands are of particular interest as the steric and electronic properties of the phosphorus donor atoms can be altered by changing the substituents of the phosphines. In addition, the ferrocene backbone of the ligands provides unique electronic and conformational flexibility to these ligands. Previous investigations in this lab have examined catalytic ring closing reactions using a series of gold compounds with bis(phosphino)ferrocene ligands, $[Au_2Cl_2(\mu\text{-PP})]$. These gold compounds were shown to react with sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, $Na[BArF_{24}]$, to generate a cationic species with the general formula $[Au_2(\mu\text{-Cl})(\mu\text{-PP})][BArF_{24}]$ that are much more efficient catalysts than the $[Au_2Cl_2(\mu\text{-PP})]$ compounds. In this study, a series

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of [$Au_2Cl_2$(μ-PP)] (μ-PP = 1,1'-bis(diphenylphosphino)ferrocene (dppf), 1,1'-bis(di*iso*-propylphosphino)ferrocene (dippf), 1,1'-bis(dicyclohexylphosphino)ferrocene (dcpf), 1,1'-bis(di*tert*-butylphosphino)ferrocene (dtbpf), 1-diphenylphosphino-1'-di*tert*-butylphosphinoferrocene (dppdtbpf) or 1,1′-bis(5-methyl-2-furanylphosphino)ferrocene (dfurpf)) compounds were examined as catalysts for the intramolecular ring-closing hydroamination of 3-(vinyloxy)propan-1-amine and the intermolecular hydroamination of phenylacetylene with a variety of phenylamine reagents. The catalytic activity of the corresponding [$Au_2$(μ-Cl)(μ-PP)][$BArF_{24}$] compounds that were generated in situ was also explored. Two new [$Au_2Cl_2$(μ-PP)] compounds with chiral bis(phosphino)ferrocene ligands (PP = 1,1'-bis(2R,5R-dimethylphospholanyl)ferrocene (R-d$^{Me}$plf) or 1,1'-bis(2S,5S-dimethylphospholanyl)ferrocene (S-d$^{Me}$plf)) were prepared, characterized spectroscopically and electrochemically, and evaluated as catalysts in the ring-closing hydroamination reaction. In addition, the X-ray structures of [$Au_2Cl_2$(μ-PP)] (PP = dppdtbpf, R-d$^{Me}$plf and S-d$^{Me}$plf) were determined.

*Keywords*: bis(phosphino)ferrocene; gold; hydroamination; catalysis; cyclic voltammetry; X-ray crystal structure

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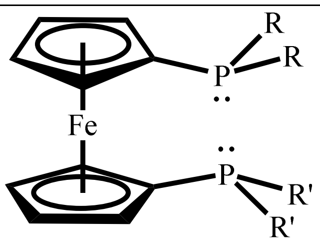
## 1. Introduction

Bis(phosphino)ferrocene compounds with a variety of organic substituents, including 1,1′-bis(diphenylphosphino)ferrocene (dppf), 1,1′-bis(di*iso*-propylphosphino)ferrocene (dippf), 1,1′- bis(dicyclohexylphosphino)ferrocene (dcpf), 1,1′-bis(di*tert*- butylphosphino)ferrocene (dtbpf), 1-(diphenylphosphino)-1′-(di*tert*- butylphosphino)ferrocene (dppdtbpf) and 1,1′-bis(bis(5-methyl-2-furanylphosphino))ferrocene (dfurpf) (Table 1), are commonly employed as ligands [1–7]. These ligands typically coordinate to transition metals, most commonly group 10, in a bidentate fashion [2,5,6,8]; however, other coordination modes are known. For example, late transition metals, in particular gold, commonly exhibit monodentate coordination of these ligands [9–12]. The coordination flexibility as well as the structural and electronic tunability of bis(phosphino)ferrocene ligands make them particularly useful ligands in a variety of catalytic applications.

**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 |

Surprisingly, gold compounds with these bis(phosphino)ferrocene ligands have received limited attention in catalysis. The ring closing reactions of (Z)-3-methylpent-2-en-4-yn-1-ol and *N*-(prop-2-yn-1-yl)benzamide were catalyzed by [$Au_2$(μ-Cl)(μ-PP)][$BArF_{24}$] (PP = dppf, dippf, dcpf, dtbpf, dppdtbpf or dfurpf) which was formed *in situ* by the reaction of the [$Au_2Cl_2$(μ-PP)] compounds with Na[$BArF_{24}$] [12]. Although one of the poorer catalysts studied, [$Au_2Cl_2$(μ-dppf)] was found to catalyze the reaction of phenylacetylene, pyridine hydrofluoride and 8-methylquinoline *N*-oxide to yield fluoromethylphenyl ketone [13]. Finally, the Sonogashira coupling reactions of terminal alkynes with aryl bromides and iodides was efficiently catalyzed with gold(I) iodide and dppf [14]. Further examination of these compounds in catalytic applications is clearly warranted.

One of the most common gold-catalyzed reactions is hydroamination, which has been reviewed extensively in recent years [15–37]. Despite the fact that gold(III)-catalyzed hydroamination of terminal alkynes had been known since 1987, it was not until 2003 that

Hayashi and Tanaka developed the first gold(I)-catalyzed intermolecular amination of alkynes with anilines to form imines [38]. Gold(I) complexes selectively activate π-bonds of alkynes via coordination of the alkyne forming a *trans*-alkenyl-gold complex intermediate, $[LAu(\eta^2\text{-}RC{\equiv}CR')]^+$, that withdraws electron density from the alkyne, making it susceptible to nucleophilic attack [23]. Various types of ligands have been examined in these gold-catalyzed reactions, but of greatest relevance to this work would be ligands containing a ferrocenyl group. A gold(I) catalyst with a N-heterocyclic carbene (NHC) ligand containing a ferrocenyl group was found to promote the intermolecular hydroamination of alkynes with anilines to form imines [39]. While the yields of these reactions were generally good, a slight downward trend in product yield was observed for more electron-rich aniline starting material. In a recent study, three different ferrocenyl phosphonite ligands were examined in the gold catalyzed hydroamination of terminal acetylenes [40]. The catalysts gave the desired imine products with a variety of acetylene and amine starting materials.

This study aims to further examine gold compounds with bis(phosphino)ferrocene ligands in catalysis. In particular, the goal was to determine the efficacy of the $[Au_2Cl_2(\mu\text{-}PP)]$ and $[Au_2Cl(\mu\text{-}Cl)(\mu\text{-}PP)]^+$ complexes in both intra- and intermolecular hydroamination reactions. In the course of this study, two new gold complexes with the chiral bis(phosphino)ferrocene ligands 1,1′-bis(2R,5R- dimethylphospholanyl)ferrocene (R-$d^{Me}$plf) and 1,1′-bis(2S,5S-dimethylphospholanyl)ferrocene (S-$d^{Me}$plf) were synthesized and characterized (Fig. 1). The X-ray crystal structures of $[Au_2Cl_2(dppdtbpf)]$, $[Au_2Cl_2(R\text{-}d^{Me}plf)]$ and $[Au_2Cl_2(S\text{-}d^{Me}plf)]$ were determined.

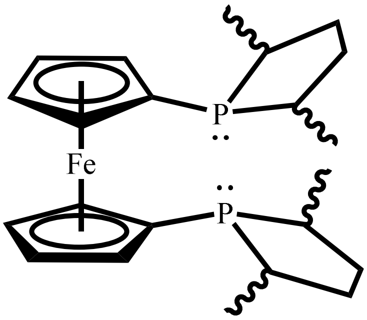


**Fig. 1.** Structure of d$^{Me}$plf ligands.

## 2. Results and discussion

The [$Au_2Cl_2$(μ-d$^{Me}$plf)] compounds were synthesized using a procedure similar to those of other [$Au_2Cl_2$(μ-bis(phosphino)ferrocene)] compounds. The compounds were characterized by $^1$H, $^{13}$C{$^1$H} and $^{31}$P{$^1$H} NMR spectroscopy. The stereocenters of the d$^{Me}$plf ligands gave these compounds complex $^1$H and $^{13}$C NMR patterns requiring the use of COSY, DEPT, HMBC and HSQC experiments to assign all of the signals. The oxidative electrochemistry of the [$Au_2Cl_2$(μ-d$^{Me}$plf)] compounds was examined in $CH_2Cl_2$. Both compounds exhibit a single chemically and electrochemically reversible wave (Fig. 2) whereas oxidation of the free d$^{Me}$plf ligands under

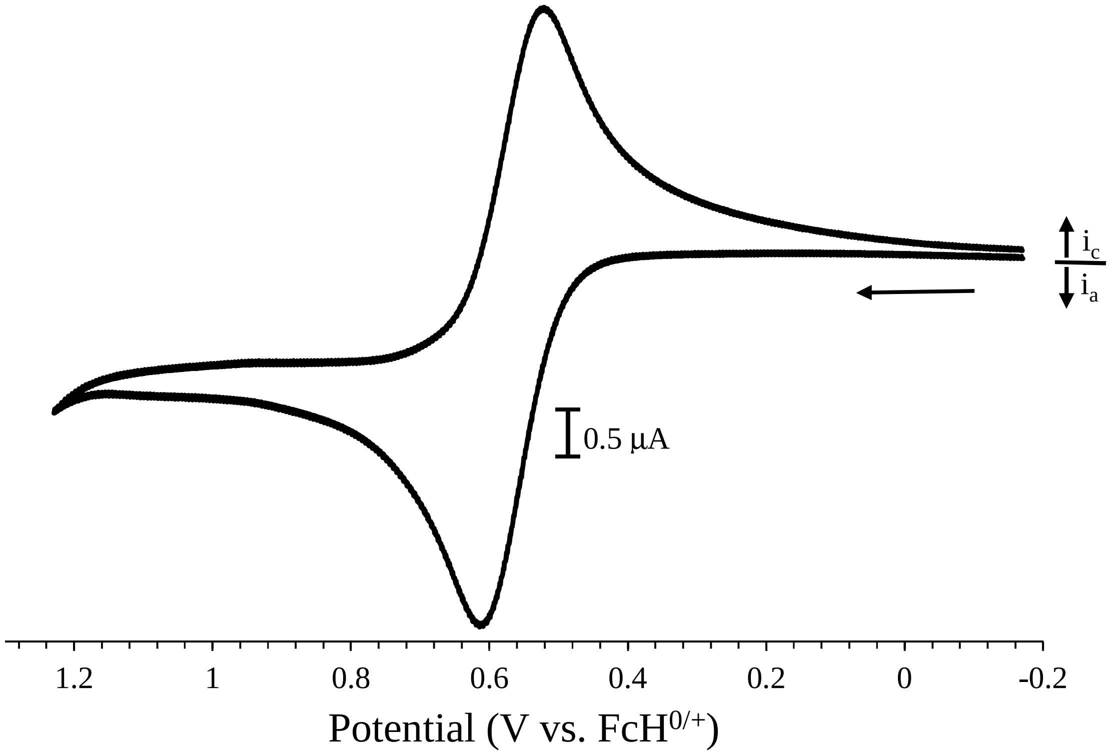


**Fig. 2.** CV scan of 1.0 mM [$Au_2Cl_2$(μ-R-$d^{Me}$plf)] in $CH_2Cl_2$ with 0.1 M [$NBu_4$][$PF_6$] as the supporting electrolyte measured at 100 mV/s.

similar conditions gave a chemically reversible wave. With respect to the iron center in these compounds, oxidation of the iron in both the free $d^{Me}$plf ligands and the [$Au_2Cl_2$(μ- $d^{Me}$plf)] compounds occurs at potentials similar to dppdtbpf and dfurpf analogs (Table 2).

**Table 2**
CV data (*E* in V vs. $FcH^{0/+}$) for ligands and [$Au_2Cl_2$(μ-PP)] compounds in $CH_2Cl_2$.

| | **Free ligand** | **[$Au_2Cl_2$(μ-PP)]** | **Reference** |
|---|---|---|---|
| dppf | 0.23[a] | 0.64 | [41] |
| dippf | 0.05[a] | 0.54 | [42] |
| dcpf | 0.02[a] | 0.52 | [43] |
| dtbpf | 0.06 | 0.56 | [44] |
| dppdtbpf | 0.11[a] | 0.59 | [41] |
| dfurpf | 0.15[a] | 0.58 | [12] |
| R-$d^{Me}$plf | 0.11[a] | 0.57 | Free ligand [45] |
| S-$d^{Me}$plf | 0.11[a] | 0.57 | Free ligand [45] |

[a] Chemically reversible waves.

The X-ray crystal structures of [$Au_2Cl_2$(μ-dppdtbpf)] (Fig. 3), [$Au_2Cl_2$(μ-R-d$^{Me}$plf)] and [$Au_2Cl_2$(μ-S-d$^{Me}$plf)] (Fig. 4) were determined and were found to be similar to those of other

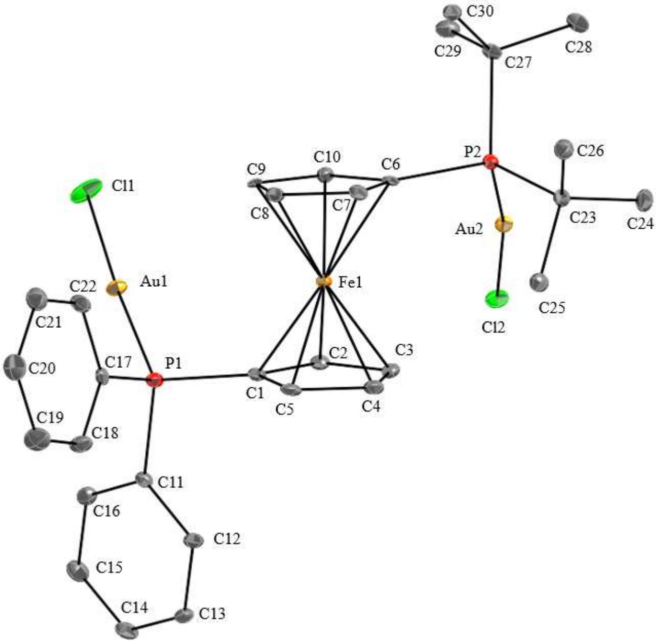
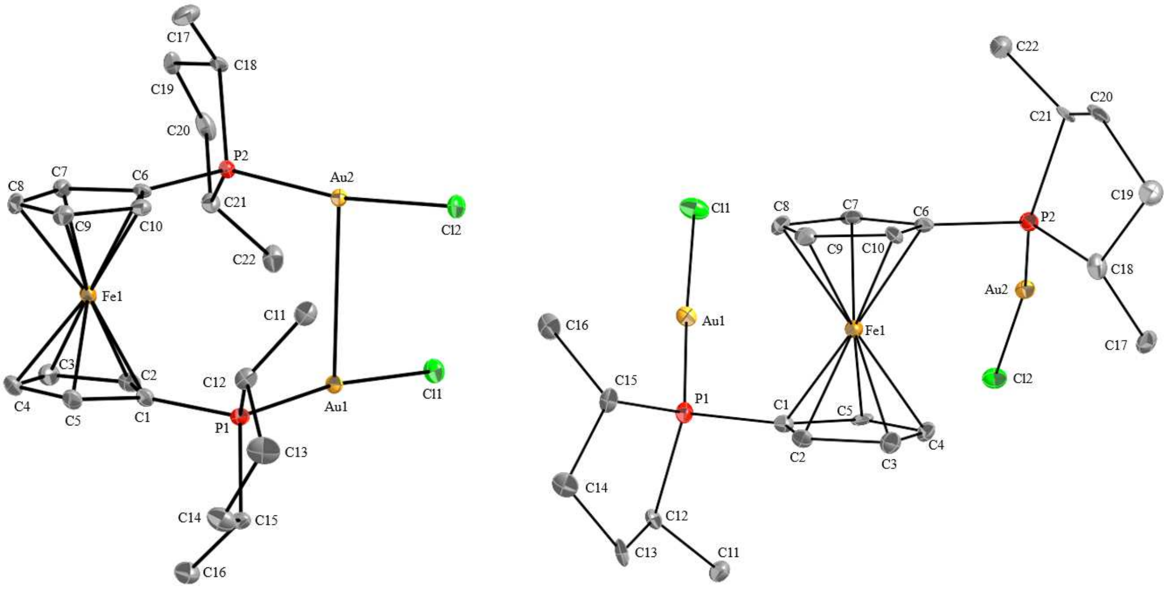


**Fig. 3.** ORTEP drawing of [$Au_2Cl_2$(μ-dppdtbpf)]. Thermal ellipsoids are drawn at the 50% probability level and the H atoms were omitted for clarity.



(a) (b)

**Fig. 4.** ORTEP drawing of (a) [$Au_2Cl_2$(μ-R-d$^{Me}$plf)] and (b) [$Au_2Cl_2$(μ-S-d$^{Me}$plf)]. Thermal ellipsoids are drawn at the 50% probability level and the H atoms were omitted for clarity.

gold compounds with 1,1'-bis(phosphino)ferrocene ligands. Selected bond lengths and angles are presented (Table 3). These structures allow for calculation of the percent buried volume (%$V_{bur}$) [46] for the ligands (Table 4). For these gold compounds the phosphine substituted with *tert*-butyl groups of dppdtbpf had a %$V_{bur}$ that was 0.2% less than the dtbpf ligand. The phenyl-substituted phosphine of dppdtbpf gave a %$V_{bur}$ that was 2.2% larger than that of dppf, potentially due to the proximity of the *tert*-butyl groups of the other phosphine. Somewhat surprisingly, the $d^{Me}$plf ligands had %$V_{bur}$ values that differed by 1.5%. In the [PdCl$_2$($\kappa^2$-$d^{Me}$plf)] compounds, the %$V_{bur}$ values for the $d^{Me}$plf ligands only differed by 0.1% [45]. A possible explanation for the difference in the gold compounds with $d^{Me}$plf ligands comes from the aurophilic interactions [47,48] between the gold centers.

**Table 3**
Selected bond lengths (Å) and angles (°) for the structures of [Au$_2$Cl$_2$(μ-dppdtbpf)], [Au$_2$Cl$_2$(μ-R-$d^{Me}$plf)] and [Au$_2$Cl$_2$(μ-S-$d^{Me}$plf)].

| | **[Au$_2$Cl$_2$(μ-dppdtbpf)]** | **[Au$_2$Cl$_2$(μ-R-$d^{Me}$plf)]** | **[Au$_2$Cl$_2$(μ-S-$d^{Me}$plf)]** |
|---|---|---|---|
| P1-Au1 | 2.2400(13) | 2.2505(19) | 2.254(4) |
| P2-Au2 | 2.2563(12) | 2.248(2) | 2.253(4) |
| Au1-Cl1 | 2.2906(14) | 2.3218(19) | 2.319(4) |
| Au2-Cl2 | 2.3182(13) | 2.3163(19) | 2.329(4) |
| $\theta^a$ | 3.74(15) | 6.1(3) | 3.1(4) |
| $X_A$-Fe-$X_B$$^b$ | 178.06(8) | 174.12(16) | 177.9(2) |
| P1-Au1-Cl1 | 176.24(4) | 171.23(6) | 174.51(9) |
| P2-Au2-Cl2 | 169.72(4) | 171.10(6) | 165.41(8) |

[a] The dihedral angle between the two $C_5$ rings.
[b] X represents the centroid of the $C_5$ rings.

**Table 4**
The percent buried volume (%$V_{bur}$) and select measurement for [Au$_2$Cl$_2$(μ-PP)] (PP = 1,1′-bis(phosphino)ferrocene) compounds.

| **Compound** | **%$V_{bur}$** | **τ(°)$^a$** | **Au···Au (Å)** | **Ref.** |
|---|---|---|---|---|
| [Au$_2$Cl$_2$(μ-dppf)] | 34.0 | 180.0(2) | 6.4589(2)$^b$ | [9] |
| [Au$_2$Cl$_2$(μ-dtbpf)] | 41.6 | -138.28(16) | 8.1373(2)$^b$ | [11] |
| [Au$_2$Cl$_2$(μ-dppdtbpf)] | 41.4$^c$<br>36.2$^d$ | 153.9(2) | 3.6073(14)$^b$ | This work |
| [Au$_2$Cl$_2$(μ-dippf)] | 38.8 | -142.4(2) | 7.2460(5)$^b$ | [10] |

| | | | | |
|---|---|---|---|---|
| [$Au_2Cl_2$(μ-dfurpf)] | 37.7 | -68.7(3) | 3.60240(19)[e] | [12] |
| [$Au_2Cl_2$(μ-R-d$^{Me}$plf)] | 38.4[f] | 61.7(5) | 3.2441(4)[e] | This work |
| [$Au_2Cl_2$(μ-S-d$^{Me}$plf)] | 36.9[f] | -139.2(7) | 3.064(3)[b] | This work |

[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 $C_5$ ring.

[b] Nearest intermolecular Au···Au distance.

[c] For -$P^tBu_2$ group.

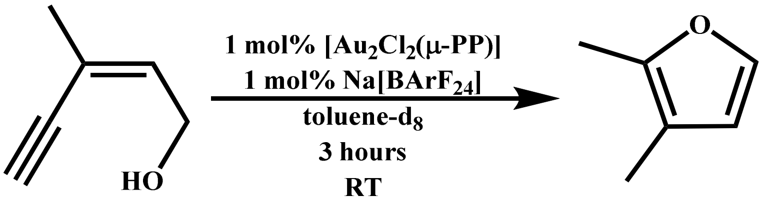
[d] for -$PPh_2$ group.

[e] Nearest intramolecular Au···Au distance.

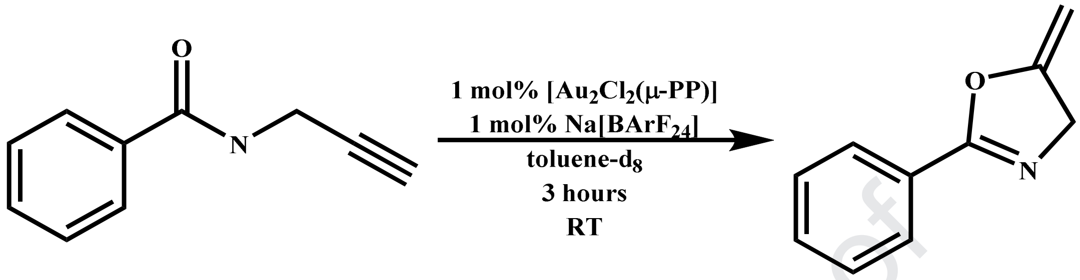
[f] Average of two values.

In the R-d$^{Me}$plf compound, there is a short intramolecular Au-Au interaction, similar to that observed in the dfurpf analog [12]. The S-d$^{Me}$plf compound displays an even shorter Au-Au interaction, but in that case the interaction is intermolecular. This interaction creates a one-dimensional polymer chain in the b-direction. The d$^{Me}$plf ligands display helical chirality based on the relative positions of the two phosphorous atoms as defined by the τ angles [49]. In these gold compounds the R-d$^{Me}$plf ligand adopts the *P*-1,2′ configuration whereas the S-d$^{Me}$plf adopts the *M*-1,4′ configuration. The *P*-1,2′ and *M*-1,4′ configurations are not helical enantiomers. From the limited data available, this appears to be unusual for d$^{Me}$plf ligands. The [$PdCl_2$(d$^{Me}$plf)] compounds are enantiomers as the R-d$^{Me}$plf compound adopts the *P*-1,2′ configuration having a τ of 44.3° [45] while the S-d$^{Me}$plf compound adopts the *M*-1,5′ configuration with a τ of -44.1° [50]. Enantiomers were also observed in the [$PtCl_2$(d$^{Me}$plf)] compounds where R-d$^{Me}$plf adopts the *P*-1,2′ configuration (τ = 43.1°) and S-d$^{Me}$plf adopts the *M*-1,5′ configuration (τ = -44.8°) [45]. The reasons for the differences between the d$^{Me}$plf ligands in the gold compounds in this report are unclear.

A previous study examined the activity of [$Au_2Cl_2$(μ-PP)] compounds with bis(phosphino)ferrocene ligands as catalysts in two different (Eq. (1 and 2)) ring-closing

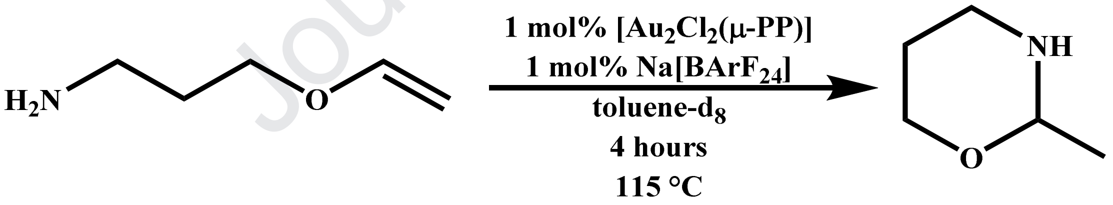


(1)



(2)

reactions [12]. The addition of Na[BArF$_{24}$] to these reactions leads to removal of a chloride ligands from the gold compounds [11], which greatly enhanced their catalytic activity [12]. However some differences based on the steric and electronic properties of the bis(phosphino)ferrocene ligands were noted. To further examine the catalytic properties of these compounds, the intramolecular hydroamination of 3-(vinyloxy)propan-1-amine was carried out using a series of [Au$_2$Cl$_2$(PP)] catalyst precursors (Eq. (3)). Previous studies have examined this ring-closing using rhodium [51–53], palladium [51–54], platinum [51,53], copper [52], zinc [52,55,56] and mercury [57] catalysts. The [Au$_2$Cl$_2$(μ-PP)] compounds in this study were all determined to be poor catalysts in this ring-closing hydroamination. However, when one equivalent of Na[BArF$_{24}$] was added along with the gold precatalyst, the ring-closing was determined to be quantitative (Table 5). Without the addition of the Na[BArF$_{24}$] the reaction mixtures maintained a yellow color during the course of the reaction, however with the addition of the Na[BArF$_{24}$] the solutions slowly turned orange-red over the course of the reaction.



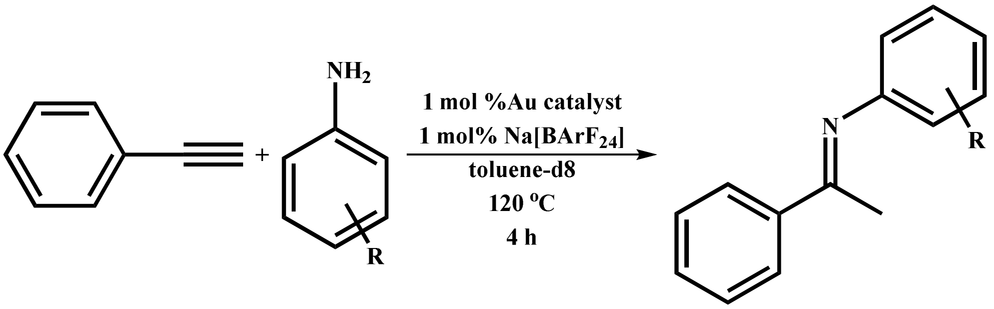
(3)

**Table 5**
Yields for the catalytic ring-closing of 3-(vinyloxy)propan-1-amine using [$Au_2Cl_2$(μ-PP)] catalysts in toluene-$d_8$ at 115 °C for 4 h.

| | **dppf** | **dippf** | **dcpf** | **dtbpf** | **dppdtbpf** | **R-d$^{Me}$plf** | **S-d$^{Me}$plf** |
|---|---|---|---|---|---|---|---|
| No Na[$BArF_{24}$] | <5% | <5% | <5% | <5% | <5% | <5% | <5% |
| 1 equiv. Na[$BArF_{24}$] | Quant. | Quant. | Quant. | Quant. | Quant. | Quant. | Quant. |

The product of this ring-closing reaction, tetrahydro-2-methyl-1,3-oxazine, possesses a chiral center, although due to the anomeric effect, there is a strong preference for the methyl group to occupy an equatorial position while the N-H occupies an axial position [58]. The gold complexes containing the chiral ligands R-d$^{Me}$plf and S-d$^{Me}$plf were effective catalysts for the ring-closing hydroamination. Addition of 0.01 mol equivalents of the NMR shift reagent tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate)europium(III) hydrate to the samples following the reaction resulted in identical downfield shifts for the proton signals of the product regardless of which catalyst was used. Addition of an additional 0.01 equivalents of the europium complex shifted the product signals further downfield. This suggests that the product formed by both catalysts adopted the same regiochemistry.

To further investigate the catalytic activity of these compounds, the intermolecular hydroamination reactions of phenylacetylene with a variety of aniline derivatives were examined (Eq. (4)). Initial investigations were made using the conditions developed for the related gold complex with a ferrocene-based ligand [39], however this gave limited formation of the desired imine. Imine formation between aniline and phenylacetylene was maximized in toluene-$d_8$ at 120 °C. Low (<5%) product formation was observed when the [$Au_2Cl_2$(μ-PP)] compounds were used



(4)

as catalyst precursors. However, when a molar equivalent of Na[BArF$_{24}$] was added to generate the [Au$_2$(μ-Cl)(μ-PP)][BArF$_{24}$] compounds in situ, the reaction mixture changed color from yellow to dark orange over the course of the reactions and the desired imines were formed in good to excellent yields (Table 6). Percent conversion to the imine products was quantified by comparing the signal for the methyl group of the imine and the signal for the methoxy group from anisole. For further verification of product formation, select reaction mixtures were analyzed by GC-MS.

**Table 6**
Yields for the catalytic hydroamination of phenylacetylene with various aniline compounds using in situ generated [Au$_2$(μ-Cl)(μ-PP)][BArF$_{24}$] catalysts in toluene-d$_8$ at 120 °C for 6 h.

| **aniline** | **dppf** | **dippf** | **dcpf** | **dtbpf** | **dppdtbpf** | **dfurpf** |
|---|---|---|---|---|---|---|
| aniline without Na[BArF$_{24}$] | <5% | <5% | <5% | <5% | <5% | <5% |
| Aniline | 35% | 75% | 89% | 91% | 62% | 36% |
| 2,6-dimethylaniline | Quant. | 93% | Quant. | Quant. | Quant. | Quant. |
| 3,5-dimethylaniline | 20% | 59% | 78% | 81% | 55% | 30% |
| 3,5-dimethylaniline[a] | 36% | 53% | 58% | 60% | 53% | 24% |
| 2,4,6-trimethylaniline | 90% | Quant. | 87% | 92% | Quant. | Quant. |
| 2,6-diiso-propylaniline | 93% | 79% | 59% | 61% | 68% | 92% |
| 4-fluoroaniline | 53% | 81% | 69% | 73% | 74% | 45% |
| 2,6-difluoroaniline | 34% | 12% | 25% | 10% | 29% | 46% |
| 3,5-difluoroaniline | 43% | 30% | 27% | 16% | 56% | 49% |
| 4-trifluoromethylaniline | 54% | 76% | 55% | 86% | 58% | 38% |
| 4-phenylaniline | 32% | 47% | 27% | 37% | 46% | 24% |

[a] Reactions performed using microwave

There appears to be a combination of steric and electronic effects of the bis(phosphino)ferrocene ligands that alters the catalytic efficiency of the [Au$_2$(μ-Cl)(μ-PP)][BArF$_{24}$] compounds. In general, higher yields seem to occur with more electron donating bis(phosphino)ferrocene ligands and more electron rich aniline reagents. This differs from the Au-NHC system in which the highest yield for hydroamination of phenylacetylene was observed with aniline, with slightly lower yields found for *p*-tolylamine and mesitylamine [39]. With electron donating substituents on the aniline starting materials, higher yields were observed with disubstitution in the 2,6- positions as opposed to the 3,5- positions. However, bulkier groups in the 2,6- positions did seem to slightly disfavor product formation. With electron withdrawing substituents on the aniline starting materials, the opposite trend was noted; disubstitution in the 3,5- positions favored product formation over the 2,6- analog. Presumably, this reaction follows a similar pathway to the previously proposed catalytic mechanism which includes a step in which the coordinated alkyne undergoes nucleophilic attack by the aniline [59]. Thus, the more electron rich anilines should be stronger nucleophiles and $[Au_2(\mu\text{-Cl})(\mu\text{-dppf})]^+$ should be the most effective catalyst as dppf is both the least electron donating and least bulky ligand employed in this study. Competitive formation of an inactive digold-σ,π-acetylide species has been observed in a related catalytic system [60]. It is possible that a similar equilibrium occurs with $[Au_2(\mu\text{-Cl})(\mu\text{-dppf})]^+$ reducing the conversion to product. Other $[Au_2(\mu\text{-Cl})(\mu\text{-PP})]^+$ catalysts may not form this additional species due to additional steric bulk preventing a second gold interaction with the alkyne.

To further study the catalytic activity of these compounds the reaction of phenylacetylene with 3,5-dimethylaniline was examined using a microwave reactor. The 3,5-dimethylaniline was chosen as it gave modest yields using thermal conditions. The yields for the microwave heated catalytic reactions were quite similar to those of the thermal reactions for all catalysts employed in this study. The significantly shorter reaction times, 15 min as opposed to 6 hr, suggest that further exploration of this method is warranted.

In summary, a series of $[Au_2Cl_2(\mu\text{-PP})]$ compounds with bis(phosphino)ferrocene ligands was explored as catalysts in an intramolecular hydroamination reaction and several closely related intermolecular hydroamination reactions. The $[Au_2Cl_2(\mu\text{-PP})]$ compounds were poor catalysts in these reactions. However, removing a chloride ligand by adding one equivalent of $Na[BArF_{24}]$ resulted in the formation of $[Au_2(\mu\text{-Cl})(\mu\text{-PP})][BArF_{24}]$ and these compounds were generally excellent catalysts in these reactions. For the intramolecular ring-closing hydroamination reaction, varying the bis(phosphino)ferrocene ligand in the gold compounds had no impact on the catalyst efficiency; all of the catalysts examined gave quantitative ring-closing. For the intermolecular hydroamination reactions, both the bis(phosphino)ferrocene ligands and the steric and electronic properties of the aniline nucleophile played a role in the catalysis.

## 3. Experimental

### *3.1. General experimental methods*

All reactions were performed under an argon atmosphere using standard Schlenk techniques at 21 (± 1) ˚C unless otherwise noted. Toluene-$d_8$, deuterochloroform, methanol and chloroform were purchased from Fisher Scientific and used without further purification. Purification of $CH_2Cl_2$ and $Et_2O$ which had been purchased from Fisher Scientific was carried out using a method similar to one previously described [61]. Phenylacetylene, anisole, 2,2′-thiodiethanol and all aniline derivatives were purchased from Aldrich and used without further purification. Tetrabutylammonium hexafluorophosphate ($[NBu_4][PF_6]$) was purchased from Aldrich and prior to use was dried under vacuum at 100 ˚C. All bis(phosphino)ferrocene ligands, ferrocene, tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate)europium(III) hydrate and $HAuCl_4 \cdot H_2O$ were purchased from Strem Chemicals and used without further purification. The 3-(vinyloxy)propan-1-amine was purchased from Combi-Blocks and used without additional purification. The gold compounds with bis(phosphino)ferrocene ligands (dppf [62], dippf [42], dcpf [43], dtbpf [44], dppdtbpf [41] and dfurpf [12]), and $Na[BArF_{24}]$ ($BArF_{24}$ = tetrakis-3,5-bis(trifluoromethyl)phenylborate) [63] were prepared according to literature methods. In the course of preparing the catalysts, single crystals of $[Au_2Cl_2(dppdtbpf)]$ were prepared by vapor diffusion of $Et_2O$ into a solution of the compound in $CH_2Cl_2$ at room temperature. NMR spectra were obtained in toluene-$d_8$ using a Bruker Avance III HD 400 FT-NMR. The $^1H$ and $^{13}C\{^1H\}$ NMR spectra were referenced using internal TMS while the $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% $H_3PO_4$. GC-MS were performed using a VG/FISONS Model MD800 Gas Chromatograph/Mass Spectrometer. Microwave reactions were performed with a CEM 300 W Discover Explorer Hybrid. Elemental analysis was performed by Midwest Microlab.

### 3.2. *Synthesis of [$Au_2Cl_2$(μ-$d^{Me}$plf)] compounds*

A solution of $HAuCl_4 \cdot H_2O$ (0.1812 g, 0.482 mmol) in a mixture of deionized water (1 mL) and methanol (5 mL) was prepared and stirred for 15 minutes at 0 °C. A solution of 2,2'-thiodiethanol (0.0217 mL) in methanol (1 mL) was added dropwise to the $HAuCl_4 \cdot H_2O$ solution, and the mixture was stirred for 15 minutes at 0 °C. A solution of the desired $d^{Me}$plf ligand (0.100 g, 0.241 mmol) was prepared in a mixture of chloroform (7.5 mL) and methanol (3 mL), and was added to the $HAuCl_4 \cdot H_2O$ solution. The reaction mixture was stirred for 18 hours, during which time the solution was allowed to warm to room temperature and a yellow precipitate formed. It was then washed with methanol (3x3 mL) and filtered. The remaining precipitate was dried in vacuo, giving the product as a yellow solid (0.1066 g (50% yield) [$Au_2Cl_2$(μ-S-$d^{Me}$plf)]; 0.1562 g (74% yield) [$Au_2Cl_2$(μ-R-$d^{Me}$plf)]). Single crystals of the [$Au_2Cl_2$(μ-$d^{Me}$plf)] compounds were grown by vapor diffusion of $Et_2O$ into a solution of the respective compound in $CH_2Cl_2$ at room temperature.

*3.2.1. Characterization of [$Au_2Cl_2$(μ-S-$d^{Me}$plf)]*. $^1H$ NMR δ (ppm): 0.87 (dd, 3H, $J$ = 16 & 8 Hz, -C$H_3$), 1.35 (m, 1H, C$H_2$), 1.47 (m, 1H, C$H_2$), 1.52 (dd, 3H, $J$ = 20 & 8 Hz, -C$H_3$), 2.11 (m, 1H, C$H_2$), 2.41 (m, 2H, C$H$ & C$H_2$), 2.62 (m, 1H, C$H$), 4.24 (AA'XX', 1H, -$C_5H_4$-$H_\alpha$), 4.72 (AA'XX', 1H, -$C_5H_4$-$H_\alpha$), 4.82 (AA'XX', 1H, -$C_5H_4$-$H_\beta$), 4.86 (AA'XX', 1H, $C_5H_4$-$H_\beta$). $^{13}C\{^1H\}$ NMR δ (ppm): 13.5 (s, DEPT +, -$CH_3$), 21.4 (d, $J$ = 8.0 Hz, DEPT +, -$CH_3$), 34.0 (d, $J$

= 1.0 Hz, DEPT -, -*C*$H_2$), 34.2 (d, *J* = 4.0 Hz, DEPT -, -*C*$H_2$), 34.2 (d, *J* = 40.0 Hz, DEPT +, -*C*H), 36.7 (d, *J* = 36 Hz, DEPT +, -*C*H), 69.3 (d, *J* = 55.3 Hz, ipso-$C_5$ ring, DEPT 0), 71.4 (d, *J* = 5.0 Hz, DEPT +, β-$C_5$ ring), 74.1 (d, *J* = 7.0 Hz, DEPT +, β-$C_5$ ring), 74.5 (d, *J* = 10.0 Hz, DEPT +, α-$C_5$), 77.1 (d, *J* = 18.1 Hz, DEPT +, α-$C_5$). $^{31}P\{^1H\}$ NMR δ (ppm): 48.8 (s). Anal. Calcd. for $C_{22}H_{32}Au_2Cl_2FeP_2$: C, 30.06; H, 3.67. Found: C, 30.37; H, 3.83.

*3.2.2. Characterization of [$Au_2Cl_2$(μ-R-$d^{Me}$plf)].* $^1H$ NMR ($CDCl_3$) δ (ppm): 0.87 (dd, 3H, *J* = 16 & 8 Hz, -C*$H_3$*), 1.36 (m, 1H, C*$H_2$*), 1.47 (m, 1H, C*$H_2$*), 1.52 (dd, 3H, *J* = 20 & 8 Hz, -C*$H_3$*), 2.10 (m, 1H, C*$H_2$*), 2.39 (m, 2H, C*H* & C*$H_2$*), 2.62 (m, 1H, C*H*), 4.24 (AA'XX', 1H, -$C_5H_4$-$H_\alpha$), 4.71 (AA'XX', 1H, -$C_5H_4$-$H_\alpha$), 4.81 (AA'XX', 1H, -$C_5H_4$-$H_\beta$), 4.85 (AA'XX', 1H, -$C_5H_4$-$H_\beta$). $^{13}C\{^1H\}$ NMR δ (ppm): 13.5 (s, DEPT +, -*C*$H_3$), 21.4 (d, *J* = 5.0 Hz, DEPT +, -C*$H_3$*), 34.0 (d, *J* = 1.0 Hz, DEPT -, -*C*$H_2$), 34.2 (d, *J* = 4.0 Hz, DEPT -, -*C*$H_2$), 34.2 (d, *J* = 40.0 Hz, DEPT +, -*C*H), 36.7 (d, *J* = 36 Hz, DEPT +, -*C*H), 69.3 (d, *J* = 62.4 Hz, ipso-$C_5$ ring, DEPT 0), 71.4 (d, *J* = 4.0 Hz, DEPT +, β-$C_5$ ring), 74.1 (d, *J* = 7.0 Hz, DEPT +, β-$C_5$ ring), 74.5 (d, *J* = 10.0 Hz, DEPT +, α-$C_5$ ring), 77.1 (d, *J* = 15.1 Hz, DEPT +, α-$C_5$ ring). $^{31}P\{^1H\}$ NMR δ (ppm): 48.8 (s). Anal. Calcd. for $C_{22}H_{32}Au_2Cl_2FeP_2$: C, 30.06; H, 3.67. Found: C, 30.33; H, 3.57.

*3.3. Electrochemistry procedure.* Cyclic voltammetry experiments were conducted using a CH Instruments Model CHI260D potentiostat at room temperature (21 ± 1 °C) under an argon atmosphere. Analyte concentrations of 1.0 mM in $CH_2Cl_2$ (10.0 mL) using 0.1 M $[NBu_4][PF_6]$ as the supporting electrolyte were used in all experiments. The working electrode was a glassy carbon disk (1.0 mm diameter) that had been polished with 1.0 μm then 0.25 μm diamond paste and rinsed with methylene chloride prior to use. A platinum wire counter electrode and a nonaqueous Ag/AgCl pseudo-reference electrode that was separated from the solution by a frit were employed in all experiments. Ferrocene was added at the end of the experiments for use as an internal reference. Background scans were subtracted from all data. 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*

Single crystals of [$Au_2Cl_2$(μ-dppdtbpf)], [$Au_2Cl_2$(μ-R-$d^{Me}$plf)] and [$Au_2Cl_2$(μ-S-$d^{Me}$plf)] were selected for analysis on a Bruker-AXS SMART Apex II X-ray diffractometer using Mo $K_\alpha$ radiation with a graphite monochromater [64]. All samples were mounted using a MiTeGen MicroMount and NVH oil. Data were collected and are reported in Table 7. Unit cells were determined by taking 12 data frames, 0.5° ϕ, in three sections of the Ewald sphere. Full hemispheres were collected on each crystal and integrated using *SAINT Plus* [65]. Data were corrected for absorption correction using *SADABS* [66]. Structures were solved by the use of intrinsic phasing [67]. Least squares refinement on $F^2$ was used for all reflections [68]. Straightforward structure solution, refinement, and the calculations of measurements were accomplished with the *APEX3* package [69]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in idealized, theoretical positions. The structure of [$Au_2Cl_2$(μ-dppdtbpf)] was solved in a centrosymmetric space group. The structures of [$Au_2Cl_2$(μ-R-$d^{Me}$plf)] and [$Au_2Cl_2$(μ-S-$d^{Me}$plf)] were solved in the non-centrosymmetric space group, $P2_12_12_1$, and refined as an inversion twin using the TWIN and BASF commands; the Flack parameter indicated the crystals were a single enantiomer. The residual electron density for [$Au_2Cl_2$(μ-S-$d^{Me}$plf)] was higher than expected at 2.52 eÅ$^{-3}$. The elemental analysis concluded that Au was properly assigned and the residual was attributed to a heavy atom absorption correction problem with Au that could not be corrected with additional face indexing. Reported measurements were made using OLEX2 [70]. The %$V_{bur}$ calculations were performed using SambVca 2.1 [71].

**Table 7**
Crystal data and structure analysis results.

| | **[$Au_2Cl_2$(μ-dppdtbpf)]** | **[$Au_2Cl_2$(μ-R-d$^{Me}$plf)]** | **[$Au_2Cl_2$(μ-S-d$^{Me}$plf)]** |
|---|---|---|---|
| formula | $C_{30}H_{36}Au_2Cl_2FeP_2$ | $C_{22}H_{32}Au_2Cl_2FeP_2$ | $C_{22}H_{32}Au_2Cl_2FeP_2$ |
| fw | 979.22 | 879.10 | 879.10 |
| crystal system | monoclinic | Orthorhombic | orthorhombic |
| space group | $P2_1/n$ | $P2_12_12_1$ | $P2_12_12_1$ |
| $a$, Å | 9.620(5) | 10.583(6) | 11.396(18) |
| $b$, Å | 17.309(8) | 14.809(8) | 14.19(2) |
| $c$, Å | 18.369(9) | 16.287(9) | 16.08(3) |
| $\alpha$, deg | 90 | 90 | 90 |
| $\beta$, deg | 98.749(16) | 90 | 90 |
| $\gamma$, deg | 90 | 90 | 90 |
| $V$, Å$^3$ | 3023(3) | 2553(2) | 2600(7) |
| Z | 4 | 4 | 4 |
| cryst. size, mm | 0.317 x 0.177 x 0.164 | 0.341 x 0.202 x 0.195 | 0.300 x 0.135 x 0.052 |
| cryst. color | orange | Orange | orange |
| radiation | 0.71073 | 0.71073 | 0.71073 |
| temp, K | 100(2) | 100(2) | 100(2) |
| $2\theta$ range, deg | 3.24-57.66 | 3.72-57.6 | 3.82-57.6 |
| data collected | | | |
| $h$ | -12 to 12 | -13 to 14 | -15 to 15 |
| $k$ | -23 to 22 | -19 to 19 | -19 to 18 |
| $l$ | -23 to 23 | -22 to 21 | -21 to 21 |
| no. of data collected | 35893 | 30548 | 31179 |
| no. of unique data | 7446 | 6259 | 6368 |
| abs. corr | SADABS | SADABS | SADABS |
| final $R$ indices | | | |
| R1 | 0.0318 | 0.0273 | 0.0392 |
| wR2 | 0.0486 | 0.0419 | 0.0579 |
| goodness of fit | 1.046 | 0.879 | 0.966 |

### *3.5. Catalytic Studies*

*3.5.1. Ring-closing hydroamination.* In an argon filled glovebox, either the desired [$Au_2Cl_2$(μ-PP)] compound (0.005 mmol) or the desired [$Au_2Cl_2$(μ-PP)] compound (0.005 mmol) and Na[$BArF_{24}$] (0.005 mmol) were added to a J Young NMR tube. Toluene-$d_8$ (0.75 mL) and 3-vinyloxy-1-propamine (0.100 mol) were added to the J Young NMR tube. The tube was sealed, removed from the glove box, placed in an aluminum block and heated to 115 °C for 4 hours. After heating the tube was removed from the heating block and allowed to cool to room temperature before $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra were obtained. Representative $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of the starting material and the reaction mixture are available in the supporting information.

### *3.5.2. Hydroamination of phenylacetylene.*

*3.5.1.1. Thermal conditions.* The hydroamination reactions using were carried out in J Young NMR tubes under an atmosphere of argon. In an argon filled glovebox, either $[Au_2Cl_2(\mu\text{-}PP)]$ (0.010 mmol) or $[Au_2Cl_2(\mu\text{-}PP)]$ (0.010 mmol) and $Na[BArF_{24}]$ (0.010 mmol) were dissolved in 1 mL toluene-$d_8$. Anisole (50 μL) was added as an internal standard. The organic reagents, phenylacetylene (0.110 mL, 1 mmol) and the desired aniline (~0.100 mL, 1.1 mmol) were then added. The tube was closed and the reactants thoroughly mixed before being inserted into an aluminum heating block and heated at 120 °C for 6 h. Upon cooling to room temperature, $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of the reaction mixtures were obtained. Representative $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of the starting materials, internal standard and the reaction mixtures along with a GC-MS trace of a reaction mixture are available in the supporting information.

*3.5.1.1. Microwave conditions.* A microwave tube was prepared with $[Au_2Cl_2(\mu\text{-}PP)]$ (0.02 mmol) and $Na[BArF_{24}]$ (0.0176 g, 0.02 mmol) along with a stir bar. In a glove box, under an atmosphere of argon, the solids were dissolved in 2 mL toluene-$d_8$. Anisole (100 μL) was added as an internal standard. Phenylacetylene (0.220 mL, 2 mmol) and 3,5-dimethylaniline (~0.27 mL, 2.2 mmol) were then added. The tube was then sealed and placed in the microwave reactor at 160 °C for 15 minutes. Upon cooling to room temperature, the reaction vessel was brought into the glovebox and a sample of the solution was transferred to an NMR tube. The $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra of the reaction mixture was obtained.

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## Appendix A. Supplementary data

Electronic Supplementary Information (ESI) available: NMR spectra for [$Au_2Cl_2$(μ-R-$d^{Me}$plf)], [$Au_2Cl_2$(μ-S-$d^{Me}$plf)] and representatives of all catalytic reactions, representative GC-MS trace for intermolecular hydroamination reaction and results of %$V_{bur}$ calculations from SambVca 2.1. CCDC 1953994 for [$Au_2Cl_2$(μ-S-$d^{Me}$plf)], 1953995 for [$Au_2Cl_2$(μ-R-$d^{Me}$plf)] and 1953996 for [$Au_2Cl_2$(μ-dppdtbpf)]. Supplementary data to this article can be found online at https://doi.org/.

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**Highlights**

- Activation of [$Au_2Cl_2$(PP)] (PP = bis(phosphino)ferrocene) by Na[B(3,5-$C_6H_3(CF_3)_2)_4]^-$
- [$Au_2$(μ-Cl)(PP)][B(3,5-$C_6H_3(CF_3)_2)_4$] catalysis of several hydroamination reactions
- [$Au_2Cl_2$(dppdtbpf)] and [$Au_2Cl_2$(d$^{Me}$plf)] ($^{Me}$pl = R or S-2,5-dimethylphosphalano) structures
- Electrochemistry of [$Au_2Cl_2$(PP)] compounds

## Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: