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**PAPER**

# P–H activation using alkynylgold substrates: steric and electronic effects†

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The susceptibility of a prototypical hydrogen phosphonate to undergo P–H activation upon treatment with alkynylgold complexes has been studied. Dynamic solution behavior was observed during reactions involving triphenylphosphine ligated substrates and was attributed to rapid phosphine exchange between the alkynylgold starting material and the gold phosphonate product. The use of bulky biaryldialkylphosphine ligands eliminated the fluxional behavior, but did not significantly slow the rate of P–H activation. Similarly, changing the supporting ligand to an N-heterocyclic carbene did not significantly slow the rate of the reaction. Despite a number of reports outlining the functionalization of propargyl alcohols using gold catalysts, incorporating these groups into the architecture of the alkynylgold substrates did not alter the product distributions. Although the chemistry tolerated a range of supporting ligands, incorporating electron donating groups into the alkyne increased the rate of the reaction while electron-withdrawing groups slowed the reaction. A possible mechanism for the process includes a transition state containing significant pi-contribution from the alkyne. Due to the high yields of gold phosphonates obtained in this chemistry as well as the mild conditions of the reactions, the interception of intermediates/catalysts by substrates or ligands containing labile P–H donors is an issue that must be circumvented when designing or developing a gold catalyzed reaction that proceeds through alkynylgold intermediates.

## Introduction

Defining the effects of steric and electronic manipulation on the susceptibility of reagents, catalysts, and intermediates to undergo a specific transformation provides critical structure activity relationships. Furthermore, designing and developing new approaches to the construction of carbon–carbon and carbon–heteroelement bonds using gold complexes as catalysts has been the subject of numerous investigations in recent years.[1–8] While many of these reactions utilize the "alkynophilic" nature of Au(I) to activate alkynes through coordination of the metal center to the π-system, a number of σ-bound alkynylgold compounds have been implicated as reactive intermediates in a range of alkyne functionalizations.[9–13] Recent examples include the gold catalyzed ethynylation of activated arenes[13] and the synthesis of propargyl amines.[10] Additionally, alkynylgold complexes are efficient transmetallating agents and have been used in palladium catalyzed cross coupling reactions as well as in the synthesis of alkynylmetal species.[14–19]

The use of secondary phosphine oxides and hydrogen phosphonates as supporting ligands has grown in popularity in recent years.[20–25] Elegant work by Ackermann demonstrated that a hydrogen phosphonate served as a supporting ligand in the palladium catalyzed coupling of aryl triflates with Grignard reagents.[26] Borner recently reported the use of hydrogen-phosphonates as ligands in rhodium catalyzed hydroformylation.[24] Li and Shen described the use of phosphine oxides as supporting ligands in Suzuki couplings.[27] Wolf outlined the use of phosphinous acid containing complexes as catalysts for cross coupling aryl and acyl halides with organozinc reagents.[28]

One of the key concerns when using secondary phosphine oxides or hydrogen phosphonates as substrates or ligands is the potential for catalyst deactivation due to competing reactions between these species and the organometallic catalysts/intermediates.[29–40] Recently Waterman reported the reactivity of metal alkyls towards primary phosphines.[41] Treatment of a triamidoamine supported zirconium species with $PhPH_2$ activated one of the P–H bonds and resulted in attachment of the phosphorus to the zirconium center along with concomitant formation of methane. Schmidbaur reported the generation of gold phosphonates by treatment of methylgold complexes with hydrogen phosphonates.[42] Our group has reported the generation of bisphosphonate palladium complexes upon addition of $HP(O)(OR)_2$ species to alkylpalladium phosphonates.[43] Glueck recently described the tandem alkynylation/arylation of primary phosphines using platinum catalysts. A key step in the catalytic reaction was a base-assisted reaction of a primary phosphine with the platinum catalyst to generate a platinum phosphide.[44]

Due to its relevance towards the development of new gold catalyzed reactions employing substrates containing labile

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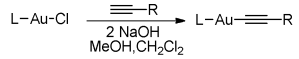
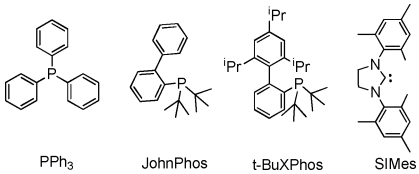
† Electronic supplementary information (ESI) available: NMR spectra for all new compounds. See DOI: 10.1039/c1dt11337b

**Table 1** Synthesis of the alkynylgold compounds used in the P–H activation reactions




| Comp. | Ligand | *R* |
|---|---|---|
| **1** | $PPh_3$ | $C_6H_5$ |
| **2** | $PPh_3$ | 4-$C_6H_4Me$ |
| **3** | $PPh_3$ | 4-$C_6H_4I$ |
| **4** | $PPh_3$ | Ferrocene |
| **5** | $PPh_3$ | $(CH_2)_3Me$ |
| **6** | $PPh_3$ | $(CH_2)_2$O-2-pyran |
| **7** | $PPh_3$ | 1-cyclohexene |
| **8** | $PPh_3$ | $CO_2Et$ |
| **9** | $PPh_3$ | Ethisterone |
| **10** | $PPh_3$ | Cyclohexanol |
| **11** | $PPh_3$ | $C(OH)Me_2$ |
| **12** | $PPh_3$ | $C(OH)H_2$ |
| **13** | JohnPhos | $C_6H_5$ |
| **14** | JohnPhos | $(CH_2)_3Me$ |
| **15** | JohnPhos | Ferrocene |
| **16** | JohnPhos | $C(OH)Me_2$ |
| **17** | JohnPhos | $C(OH)H_2$ |
| **18** | tBuXPhos | $C_6H_5$ |
| **19** | tBuXPhos | $(CH_2)_3Me$ |
| **20** | tBuXPhos | Ferrocene |
| **21** | tBuXPhos | Cyclohexanol |
| **22** | SIMes | $(CH_2)_3Me$ |
| **23** | SIMes | 4-$C_6H_4Me$ |
| **24** | SIMes | Ferrocene |
| **25** | SIMes | Cyclohexene |
| **26** | SIMes | $(CH_2)_2$O-2-pyran |
| **27** | SIMes | $CO_2Me$ |
| **28** | SIMes | Ethisterone |
| **29** | SIMes | Cyclohexanol |
| **30** | SIMes | $C(OH)Me_2$ |
| **31** | SIMes | $C(OH)H_2$ |

P–H bonds either as substrates or as supporting ligands, the susceptibility of discrete alkynylgold complexes to promote P–H activation has been determined. In addition, the electronic and steric tolerance of the reaction has been established through substrate and supporting ligand manipulation.

## Results and discussion

### Preparation of alkynylgold complexes

The alkynylgold substrates were prepared by treatment of LAuCl (L = $PPh_3$, JohnPhos, tBuXPhos, SIMes) precursors[45–48] with terminal alkynes and NaOH in $CH_2Cl_2$/MeOH (Table 1).[49–51] A variety of functionalized alkynes including propargyl alcohols and steroids were successfully employed in these reactions. In addition to changing the steric and electronic structure of the alkynes, several different supporting ligands were incorporated into the alkynylgold complexes. Bulky biaryldialkylphosphines as well as an N-heterocyclic carbene (NHC) were also used as donors for the gold center. This synthetic methodology was tolerant of the bulky biaryldialkylphosphines as well as the SIMes donor and moderate to high yields of the alkynylgold complexes were obtained. While triphenylphosphine ligated examples were successfully purified by multiple recrystallizations (pentane diffusion into saturated benzene solutions), several of the SIMes, JohnPhos, and tBuXPhos examples displayed significant solubility in hexane and were purified by column chromatography. All of the alkynylgold complexes were stable white solids with the exception of the ferrocene containing species which were isolated as orange crystals. In solution, the triphenylphosphine ligated compounds displayed sharp singlets between 41–43 ppm in the $^{31}P\{^1H\}$ NMR spectrum, while the JohnPhos and tBuXPhos ligated complexes exhibited sharp resonances between 63 and 65 ppm. Compounds containing the SIMes donor displayed the expected resonances in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra with the carbene carbon observed between 209 and 211 ppm.

### P–H activation studies

To determine a baseline for the reactivity of the alkynylgold complexes towards $HP(O)(OR)_2$ species, we investigated a model system comprised of $Ph_3PAuC{\equiv}C$–Bu (**5**) as the representative alkynylgold complex and diethylphosphite as the prototypical hydrogen phosphonate. During the initial phases of the project, the effect of solvent on the rate and outcome of this reaction was investigated. In $CDCl_3$ solution, treatment of **5** with 1 equiv of diethylphosphite (1.6 mM, 90 °C) smoothly generated the gold phosphonate in near quantitative yields along with concomitant formation of 1-hexyne. No attempts were made to remove the air or adventitious moisture from these reactions.

Preliminary concerns about side reactions between the alkynylgold compounds and small amounts of acid from the $CDCl_3$ were unwarranted. Only minimal amounts of $Ph_3PAuCl$ (<4%) were observed after heating reactions in $CDCl_3$ for several days. Changing the solvent to $C_6D_6$ resulted in a significant increase in the rate of the reaction. At 90 °C (in $C_6D_6$), the P–H activation process was complete in a few minutes. Similar to the reactions in $CDCl_3$, only trace amounts of secondary products were observed. Lowering the reaction temperature to 64 °C still afforded excellent conversions in $C_6D_6$ solution.

Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy in either $CDCl_3$ or $C_6D_6$ revealed dynamic solution behavior during the course of the reaction (Fig. 1). Although the isolated alkynylgold species (**5**) displayed a sharp singlet in either $CDCl_3$ or $C_6D_6$, significant broadening in the signal was observed upon addition of diethylphosphite (~10 min). As the P–H activation progressed, the signal for **5** continued to broaden and merged with the phosphine resonance from $Ph_3PAuP(O)(OEt)_2$. Additionally, instead of the expected set of doublets, broad singlets were observed. These collapsed doublets are likely to be the result of phosphine exchange between the starting alkynylgold species and the gold phosphonate. It was also possible that the diethylphosphite tautomerized and coordinated/exchanged with the triphenylphosphine bound to **5**. However, the resonance for the diethylphosphite was quite sharp while the signal for **5** broadened (Fig. 1) suggesting that it did not play a role in the dynamic process. Another possibility was a reversible exchange process that generated $(PPh_3)_2Au^+$ and $Au(P(O)(OEt)_2)_2^-$. However, once the starting alkynylgold complex was fully consumed

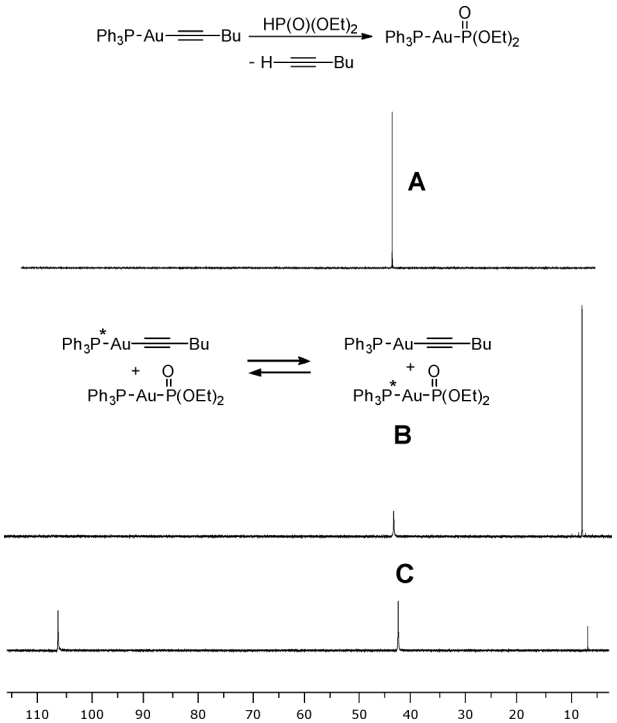



**Fig. 1** Dynamic solution behavior observed while monitoring the P–H activation involving complex **5** using $^{31}P\{^{1}H\}$ NMR spectroscopy ($C_6D_6$ at 64 °C). A) No diethylphosphite. B) 10 min. C) 14 h.

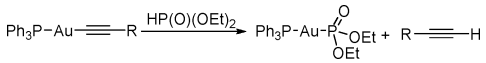
(or the gold phosphonate was isolated/purified), sharp doublets for the two phosphorus centers in $Ph_3PAuP(O)(OEt)_2$ were observed.

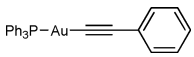
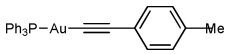
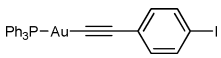
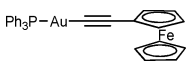
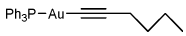
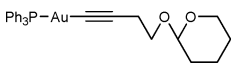
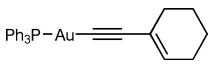
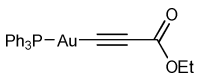
Once conditions for a successful P–H activation were found for **5**, several functionalized alkynylgold species (**1–8**) were screened in the NMR experiments (Table 2). The first manipulation of the alkyne electronics involved changing the donating alkyl group for slightly withdrawing aromatic groups (**1–3**). After stirring for 14 h at 64 °C, analysis of the $^{1}H$ and $^{31}P\{^{1}H\}$ NMR spectra from reactions involving **1–3** revealed that slightly less of the gold phosphonate had been formed (~80%). Heating the reaction for an additional 5 h achieved >90% conversion. The ferrocene derivative (**4**) also required slightly longer reaction times needed to reach >90% conversion (~20 h).[52] The most electron withdrawing group screened in this chemistry was an ester (**8**). Incorporating this group into the alkynylgold compound dramatically decreased the rate of the P–H activation reaction. After stirring for 14 h at 64 °C in $C_6D_6$, only 40% of **8** had been converted into the gold phosphonate.

All of the triphenylphosphine ligated examples exhibited the dynamic solution behavior described above. Correlating this data revealed that alkyne substituents bearing electron donating groups were more susceptible to P–H activation than those containing electron withdrawing groups.

One of the issues with the P–H activation chemistry described above was the dynamic solution behavior observed during the course of the reaction. Eliminating this exchange process would be ideal and one approach to slowing the intermolecular reaction was to incorporate large bulky ligands around the gold center. In addition to determining if these complexes slowed the exchange process, they could also be used to probe whether or not

**Table 2** P–H activation involving $Ph_3PAuC{\equiv}CR$ species[a]




| | alkynylgold complex | (Conv.) yield[b] |
|---|---|---|
| 1 |  | (95)89 |
| 2 |  | (94)87 |
| 3 |  | (87)79 |
| 4 |  | (88)81 |
| 5 |  | (99)95 |
| 6 |  | (91)83 |
| 7 |  | (87)82 |
| 8 |  | (40) |

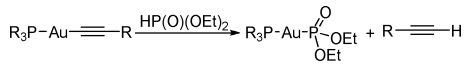
[a] Reactions carried out in $C_6D_6$ (8.0 mM) at 64 °C under air. [b] Reaction yields based upon isolated material. The numbers in parentheses represent NMR conversions as determined using internal standards (anisole or hexamethylbenzene).

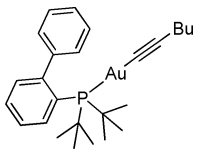
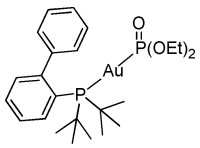
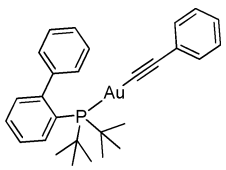
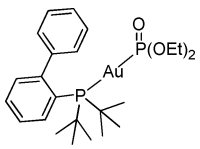
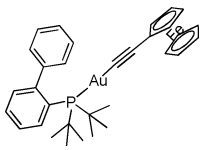
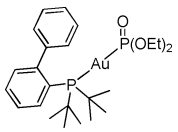
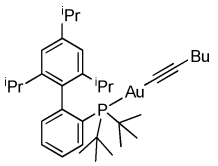
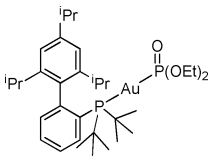
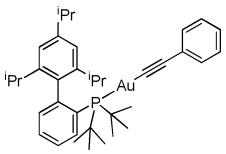
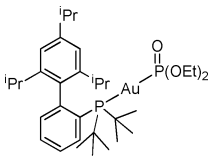
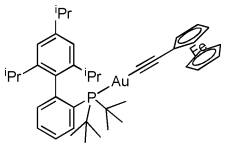
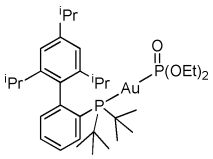
bulky ligands could inhibit the P–H activation process. Biaryldialkylphosphine ligands were selected as the bulky phosphine ligands (Tables 1 and 3) due to their remarkable air stability,[53] ready availability,[54] and propensity to promote transition metal catalyzed cross coupling reactions.[54–62]

Once isolated, the alkynylgold complexes incorporating bulky phosphine ligands were screened in the P–H activation reaction. Similar to the studies involving **1–8**, diethylphosphite was used as the prototypical P–H donor. The results of these P–H activation studies are summarized in Table 3. Treatment of **13–15** and **18–20** with $HP(O)(OEt)_2$ in $C_6D_6$ at 64 °C generated (JohnPhos)AuP(O)(OEt)$_2$ and (tBuXPhos)AuP(O)(OEt)$_2$ in excellent yields. In contrast to the dynamic solution behavior observed using triphenylphosphine as the supporting ligand (Fig. 1) no broadening of the signals in the $^{1}H$ or $^{31}P\{^{1}H\}$ NMR spectra were observed in the reactions involving the bulky biaryldialkylphosphines (Fig. 2). Thus, the addition of the bulky ligands successfully inhibited the intermolecular exchange process (at least on the NMR timescale). Analyzing the reaction data revealed that the bulky phosphine ligands did not appear to significantly impede the rate of P–H activation. High yields of the gold phosphonates were obtained in virtually the same time frame as when triphenylphosphine was used as the supporting ligand.

In an effort to further explore the scope of this reaction, an NHC ligand was incorporated into the alkynylgold complexes. Carbenes are excellent σ-donors and have been used as supporting ligands for metal centers in a range of organic

**Table 3** P–H activation involving alkynylgold species containing bulky groups[a]




| | alkynylgold complex | gold phosphonate | (Conv.) yield[b] |
|---|---|---|---|
| 1 |  |  | (98)89 |
| 2 |  |  | (88)85 |
| 3 |  |  | (89)78 |
| 4 |  |  | (97)81 |
| 5 |  |  | (95)80 |
| 6 |  |  | (88)75 |

[a] Reactions carried out in $C_6D_6$ (8.0 mM) at 64 °C under air. [b] Reaction yields based upon isolated material. The numbers in parentheses represent NMR conversions as determined using internal standards (anisole or hexamethylbenzene).

transformations.[63–69] The alkynylgold species containing carbene donors were generated using similar protocols to those described above. Once in hand, the (SIMes)AuC≡CR complexes (**22–27**) were treated with 1 equiv $HP(O)(OEt)_2$ in $C_6D_6$ at 64 °C. In most cases, treatment of these compounds with diethylphosphite smoothly generated (SIMes)AuP(O)$(OEt)_2$ in high yields (Table 4). (SIMes)AuP(O)$(OEt)_2$ was isolated as a white crystalline solid that exhibited a $^2J_{C-P}$ of 170 Hz between the carbene carbon and the phosphorus center. Similar to the approach used in the reactions above, the electronic scope of the reaction was investigated by changing the substituents attached to the alkyne. Incorporating electron donating substituents resulted in the fastest reaction rates.

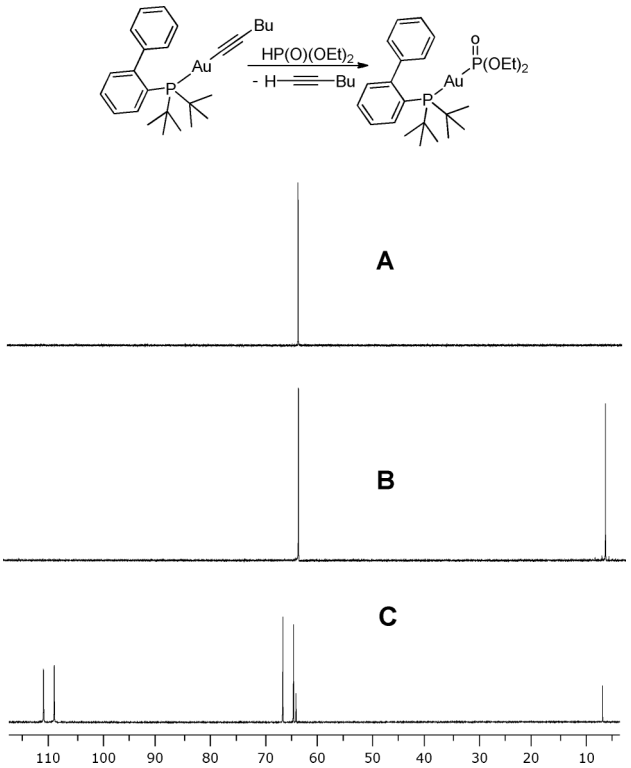



**Fig. 2** No dynamic solution behavior observed while monitoring the P–H activation involving complex **14** using $^{31}P\{^1H\}$ NMR spectroscopy ($C_6D_6$ at 64 °C). A) No diethylphosphite. B) 10 min. C) 14 h.

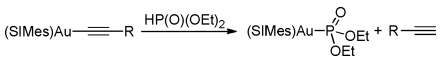
Adding electron withdrawing groups resulted in sluggish chemistry and low conversions were observed. These results were similar to the findings when compounds **1–8**, **13–15**, and **18–20** were screened.

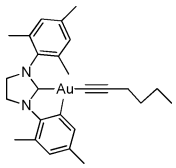
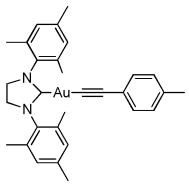
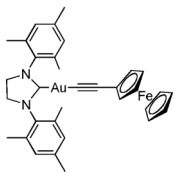
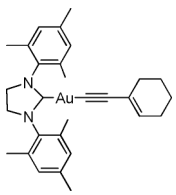
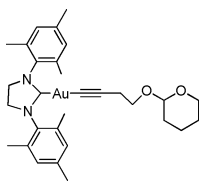
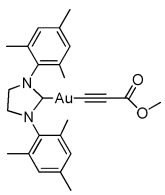
To investigate the functional group tolerance, model complexes incorporating a range of propargyl alcohols were constructed using the synthetic methodology described above. Reactions involving these compounds could deviate significantly from the clean P–H activation chemistry observed with LAuC≡CR (R = alkyl, aryl) species as gold complexes are known to catalyze reactions involving propargyl alcohols.[70–73] Furthermore, propargyl alcohols react with a variety of compounds containing labile P–H groups to generate a number of different products through dehydration,[74] substitution,[75] and hydrophosphinylation.[76,77] To investigate whether or not the propargyl alcohol could circumvent the P–H activation through alternate chemical reaction pathways or inhibit the process by sequestering the phosphite through simple hydrogen bonding, a range of alkynylgold complexes containing triphenylphosphine (**9–12**), JohnPhos (**16**, **17**), tBuXPhos (**21**), and SIMes(**28–31**) were generated (Table 1) and screened for reactivity towards diethylphosphite.

The alkynylgold complexes containing propargyl alcohols were treated with diethylphosphite in $C_6D_6$ at 64 °C (Table 5). Despite the potential for a range of products due to substitution, elimination, and addition, the propargyl alcohol containing substrates underwent smooth P–H activation with no indication of secondary reaction products. Furthermore, the identity of the groups attached to the propargyl alcohol did not significantly affect the P–H activation process. Complexes containing bulky steroids and 5–6

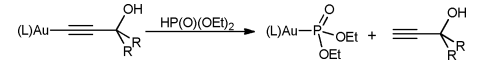
**Table 4** P–H activation involving (SIMes)AuC≡CR species[a]

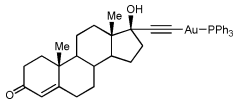
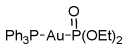
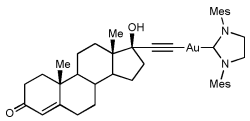
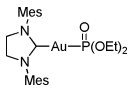
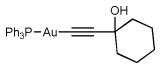
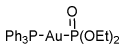
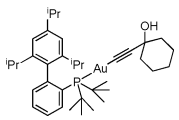
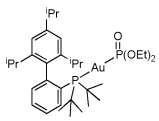
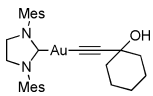
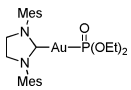
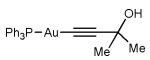
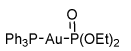
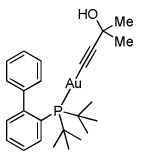
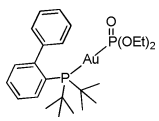
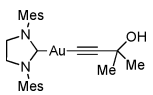
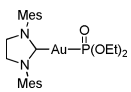
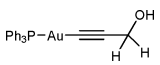
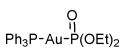
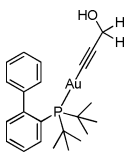
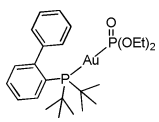
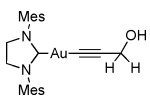
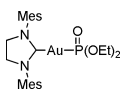



| | alkynylgold complex | (Conv.) yield[b] |
|---|---|---|
| **1** |  | 95 |
| **2** |  | 90 |
| **3** |  | 86 |
| **4** |  | 78 |
| **5** |  | 87 |
| **6** |  | (20) |

[a] Reactions carried out in $C_6D_6$ (8.0 mM) at 64 °C under air. [b] Conversion based upon consumption of starting alkynylgold complex. Reaction yields based upon isolated gold phosphonate.

**Table 5** P–H activation using alkynylgold substrates containing propargyl alcohols[a]

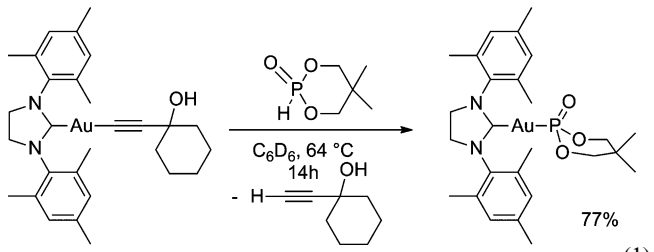



| | alkynylgold complex | gold phosphonate | (Conv.) yield[b] |
|---|---|---|---|
| **1** |  |  | (95) |
| **2** |  |  | (90) |
| **3** |  |  | (89)85 |
| **4** |  |  | (95)76 |
| **5** |  |  | 91[c] |
| **6** |  |  | (84)77 |
| **7** |  |  | (93)90 |
| **8** |  |  | 95[c] |
| **9** |  |  | (88)75 |
| **10** |  |  | (91)86 |
| **11** |  |  | 89[c] |

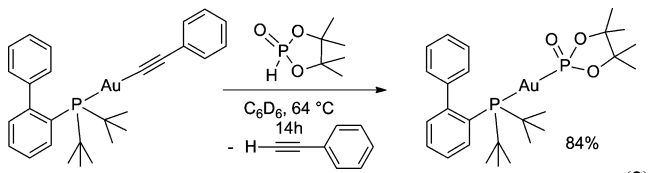
[a] Reactions carried out in $C_6D_6$ (8.0 mM) at 64 °C under air. [b] Reaction yields based upon isolated material. The numbers in parentheses represent NMR conversions as determined using internal standards (anisole or hexamethylbenzene). [c] NMR conversions unavailable due to the low solubility of the gold phosphonate.

membered rings were all converted into the corresponding gold phosphonates. As shown in Table 5, changing from triphenylphosphine to a bulky biaryldialkylphosphine or a carbene did not have a significant effect on the P–H activation process. Monitoring the reaction mixtures using NMR spectroscopy revealed that the triphenylphosphine ligated examples (**9–12**) exhibited the same dynamic solution behavior observed with compounds **1–8**. Reactions involving the bulky biaryldialkylphosphine ligands or SIMes did not exhibit any dynamic behavior and sharp signals were observed in the NMR spectra. Thus, the P–H activation proceeded without any inhibition due to the presence of the propargyl alcohol.

To probe the reactivity of the alkynylgold compounds towards other hydrogen phosphonates, several additional substrates were screened under the P–H activation conditions (eqn 1,2). Treatment of (JohnPhos)AuC≡C–Ph and and (SIMes)AuC≡C-cyclohexan-1-ol with cyclic hydrogen phosphonates ($C_6D_6$, 14 h) cleanly generated the gold phosphonates in high yields. As with the reactions involving diethylphosphite, the reaction chemistry was very clean and only trace amounts of secondary products were observed in these reactions.




(1)




(2)

There are several possibilities for the mechanism of this reaction. One possibility entails oxidative addition of the P–H bond across the gold center to generate a gold(III) species. Reductive elimination would afford the observed products. Our own attempts to effect an oxidative addition reaction between aryl halides and gold substituted ethynylsteroids[78] were unsuccessful and only starting materials were recovered. These observations were supported by a recent report which outlined problematic oxidative addition reactions of aryl halides to gold(I) centers.[17] The electronic effects observed in these reactions suggest the presence of a transition state containing coordination of the P–H donor to the metal complex such that there is partial overlap of the alkyne π-system while simultaneously labilizing the gold–carbon bond.[79,80] Electron donating groups would enhance this π-contribution and accelerate the reaction while electron withdrawing groups would result in sluggish P–H activation.

## Conclusions

Discrete alkynylgold complexes react with hydrogen phosphonates under mild conditions to generate gold phosphonates and a terminal alkyne through P–H activation. The chemistry tolerated a wide range of functional groups including propargyl alcohols. Increasing the steric bulk of the supporting ligand did not significantly inhibit or change the outcome of the reactions. A significant electronic effect was found and correlated with the identity of the organic fragment on the alkyne. Electron donating substituents exhibited faster rates while substrates containing electron withdrawing groups were sluggish under the reaction conditions. Due to the high yields of gold phosphonates obtained in this chemistry as well as the mild conditions of the reactions, the interception of intermediates/catalysts by reagents containing labile P–H donors is an issue that must be circumvented when designing or developing a gold catalyzed reaction that proceeds through alkynylgold intermediates and involves hydrogen phosphonates as supporting ligands or substrates.

## Experimental

### General considerations

Diethyl ether, dichloromethane, THF, and hexane were dried using a Grubbs-type solvent purification system. All reagents were obtained from Acros and Aldrich and used as received with the exception of diethylphosphite which was distilled twice before use. Elemental analyses were performed by Midwest Microlabs. NMR spectra were collected on a Varian 600 or 400 MHz NMR spectrometer. $^1$H and $^{13}$C chemical shifts were determined by reference to tetramethylsilane. $^{31}$P NMR spectra were referenced relative to external phosphoric acid. All coupling constants are given in hertz. The LAuCl (L = phosphine, SIMes) precursors were prepared by displacement of dimethylsulfide from $Me_2AuCl$ by added L, and their NMR spectra compared with literature values.[45–48] Known compounds **1**, **2**, **4**, **5**, **9**, **10**, and **12** were prepared following the general procedures outlined below, and their NMR spectra compared with reported literature values (see ESI†).[78,81–84]

**General procedure for preparation of alkynyl gold complexes[45–48].** A round bottom flask (50 mL) was charged with the LAuX (X = Cl; L = $PPh_3$, JohnPhos, tBuXPhos, SIMes) precursor, and 2 equiv of NaOH. After evacuating and refilling the flask with nitrogen, methanol (10 mL) was added by syringe, and the reaction mixture was stirred for 20 min. Dichloromethane was added until a homogeneous solution was obtained. Liquid alkynes were added directly to this solution while solid alkynes were dissolved in MeOH/$CH_2Cl_2$ prior to addition. The reaction was covered in foil and stirred overnight followed by removal of the volatiles under vacuum and extraction of the residue with benzene (10 mL). After filtration to remove insoluble salts, the desired alkynylgold complexes were purified by recrystallization or column chromatography

**Preparation of 3.** The general procedure was followed with $Ph_3PAuCl$ (0.20 g, 0.404 mmol), 4-iodoethynylbenzene (0.093 g, 0.408 mmol), NaOH (0.032 g, 0.80 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). Recrystallization by diffusion of pentane into a saturated benzene solution afforded 0.18 g (64.9%) of the title compound as white needles. Anal. Calcd for $C_{26}H_{19}AuIP$: C, 45.50; H, 2.79. Found: C, 45.13; H, 3.42. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 7.58–7.49 (m, 11H, Ar–H), 7.48–7.43 (m, 6H, Ar–H), 7.22 (AA′BB′, 2H, Ar–H).$^{13}$C{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 137.1 (s, Ar–CH), 134.3 (d, $J$ = 13.4, Ar–CH), 133.8 (d, $J$ = 142.1, ≡C–), 134.0 (s, Ar–CH), 131.6 (d, $J$ = 2.9, Ar–CH), 129.7 (d, $J$ = 56.1, quat), 129.2 (d, $J$ = 11.2, Ar–CH), 124.4 (d, $J$ = 2.9, quat), 103.1 (d, $J$ = 26.2, ≡C–), 92.2 (s, quat). $^{31}$P{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 42.2 (s).

**Preparation of 6.** The general procedure was followed with $Ph_3PAuCl$ (0.20 g, 0.404 mmol), 2-(3-butynyloxy)tetrahydro-2*H*-pyran (48 μL, 0.408 mmol), NaOH (0.032 g, 0.80 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). Recrystallization by diffusion of pentane into a saturated benzene solution afforded 0.21 g (84.8%) of the title compound as white needles. Anal. Calcd for

$C_{27}H_{28}AuO_2P$: C, 52.95; H, 4.61. Found: C, 52.58; H, 4.38. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 7.54–7.47 (m, 9H, $-C_6H_5$), 7.44–7.41 (m, 6H, $-C_6H_5$), 4.65 (t, 1H, $J$ = 4.0, –CH–), 3.88 (m, 2H, $-CH_2-$), 3.66 (m, 1H, $-CH_2-$), 3.49 (m, 1H, $-CH_2-$), 2.70 (t, 2H, $J$ = 7.8, $-CH_2-$), 1.83 (m, 1H, $-CH_2-$), 1.71 (m, 1H, $-CH_2-$), 1.61–1.49 (m, 4H, $-CH_2-$).$^{13}$C{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 134.3 (d, $J$ = 13.6, $-C_6H_5$), 131.5 (d, $J$ = 2.3, $-C_6H_5$), 129.9 (d, $J$ = 55.5, *–ipso–*$C_6H_5$), 129.1 (d, $J$ = 11.2, $-C_6H_5$), 121.1 (d, $J$ = 142.2, ≡C–), 101.2 (d, $J$ = 27.0, ≡C–), 98.7 (s, –CH–), 67.0 (s, $-CH_2-$), 62.2 (s, $-CH_2-$), 30.6 (s, $-CH_2-$), 25.5 (s, $-CH_2-$), 21.3 (d, $J$ = 2.3, $-CH_2-$), 19.6 (s, $-CH_2-$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 42.3 (s).

**Preparation of 7.** The general procedure was followed with ($Ph_3P$)AuCl (0.20 g, 0.404 mmol), 1-ethynylcyclohexene (47.6 µL, 0.405 mmol), NaOH (0.032 g, 0.80 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). Recrystallization by diffusion of pentane into a saturated benzene solution afforded 0.15 g (65.7%) of the title compound as white needles. Anal. Calcd for $C_{26}H_{24}AuP$: C, 55.33; H, 4.29. Found: C, 55.61; H, 4.57. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 7.55–7.48 (m, 9H, $-C_6H_5$), 7.44–7.42 (m, 6H, $-C_6H_5$), 6.13 (m, 1H, ═CH–), 2.21 (m, 2H, $-CH_2-$), 2.09 (m, 2H, $-CH_2-$), 1.62 (m, 2H, $-CH_2-$), 1.56 (m, 2H, $-CH_2-$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 134.4 (d, $J$ = 13.6, $-C_6H_5$), 133.5 (s, ═*C*H–), 131.5 (d, $J$ = 2.7, $-C_6H_5$), 129.9 (d, $J$ = 55.6, *–ipso–*$C_6H_5$), 129.1(d, $J$ = 11.3, $-C_6H_5$), 127.8 (d, $J$ = 141.9, ≡C–), 121.3 (s, quat), 106.5 (d, $J$ = 26.2, ≡C–), 30.4 (s, $-CH_2-$), 25.8 (s, $-CH_2-$), 22.6 (s, $-CH_2-$), 21.7 (s, $-CH_2-$).$^{31}$P{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 42.4 (s).

**Preparation of 8.** The general procedure was followed with $Ph_3PAuCl$ (0.20 g, 0.404 mmol), ethylpropiolate (41 µL, 0.405 mmol), NaOH (0.032 g, 0.80 mmol), $CH_2Cl_2$ (5 mL), and EtOH (10 mL). Recrystallization by diffusion of pentane into a saturated benzene solution afforded 0.14 g (62.2%) of the title compound as white needles. Anal. Calcd for $C_{23}H_{20}AuO_2P$: C, 49.65; H, 3.62. Found: C, 49.88; H, 3.15. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 7.55–7.43 (m, 15H, Ar–H), 4.20 (q, 2H, $J$ = 7.0, $-OCH_2-$), 1.29 (t, 3H, $J$ = 7.1, $-CH_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 153.5 (d, $J$ = 2.9, C═O), 134.3 (d, $J$ = 141.3, ≡C–), 134.3 (d, $J$ = 14.0, $-C_6H_5$), 131.8 (d, $J$ = 2.3, $-C_6H_5$), 129.3 (d, $J$ = 11.8, $-C_6H_5$), 129.2 (d, $J$ = 57.2, *ipso–*$C_6H_5$), 93.6 (d, $J$ = 25.8, ≡C–), 61.2 (s, $-OCH_2-$), 14.2 (s, $-CH_3$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 41.3 (s).

**Preparation of 11.** The general procedure was followed with $PPh_3AuCl$ (0.20 g, 0.404 mmol), 2-methyl-3-butyn-2-ol (39.2 µL, 0.404 mmol), NaOH (0.032 g, 0.80 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). Recrystallization by diffusion of pentane into a saturated benzene/$CH_2Cl_2$ solution afforded 0.13 g (59.3%) of the title compound as white needles. Anal. Calcd for $C_{23}H_{22}AuOP$: C, 50.93; H, 4.09. Found: C, 50.92; H, 4.08. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 7.55–7.48 (m, 9H, $-C_6H_5$), 7.46–7.42 (m, 6H, $-C_6H_5$), 1.59 (s, 6H, $-CH_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 134.3 (d, $J$ = 14.0, $-C_6H_5$), 131.5 (d, $J$ = 2.3, $-C_6H_5$), 129.8 (d, $J$ = 54.9, quat), 129.1 (d, $J$ = 11.3, $-C_6H_5$), 121.3 (d, $J$ = 141.6, ≡C–), 109.5 (d, $J$ = 25.5, ≡C–), 65.6 (s, quat), 32.6 (s, $-CH_3$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 42.3 (s)

**Preparation of 13.** The general procedure was followed with (JohnPhos)AuCl (0.20 g, 0.377 mmol), phenylacetylene (41.4 µL, 0.377 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–60 : 40) to afford 0.19 g (84.5%) of a white powder. Anal. Calcd for $C_{28}H_{32}AuP$: C, 56.38; H, 5.41. Found: C, 56.45; H, 5.40. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 7.87 (m, 1H, Ar–CH), 7.56–7.44 (m, 7H, Ar–CH), 7.29 (m, 1H, Ar–CH), 7.24–7.14 (m, 5H, Ar–CH), 1.42 (d, 18H, $J$ = 14.4, $-PC(CH_3)_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 150.3 (d, $J$ = 15.2, quat), 142.4 (d, $J$ = 6.2, quat), 134.3 (d, $J$ = 1.2, Ar–CH), 134.1 (d, $J$ = 131.8, ≡C–), 133.1 (d, $J$ = 7.2, Ar–CH), 132.2 (s, Ar–CH), 130.2 (d, $J$ = 2.3, Ar–CH), 129.2 (s, Ar–CH), 129.0 (s, Ar–CH), 128.1 (s, Ar–CH), 127.7 (s, Ar–CH), 127.6 (d, $J$ = 39.8, quat), 126.6 (d, $J$ = 5.6, Ar–CH), 126.2 (d, $J$ = 2.7, quat), 126.0 (s, Ar–CH), 102.2 (d, $J$ = 23.5, ≡C–), 37.5 (d, $J$ = 22.3, $PC(CH_3)_3$), 31.1 (d, $J$ = 7.2, $PC(CH_3)_3$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 64.4 (s).

**Preparation of 14.** The general procedure was followed with (JohnPhos)AuCl (0.20 g, 0.377 mmol), 1-hexyne (43.3 µl, 0.377 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–60 : 40) to afford 0.16 g (73.7%) of a white powder. Anal. Calcd for $C_{26}H_{36}AuP$: C, 54.17; H, 6.29. Found: C, 54.29; H, 6.25. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 7.84 (m, 1H, Ar–H), 7.45 (m, 5H, Ar–H), 7.26 (m, 1H, Ar–H), 7.14 (m, 2H, Ar–H), 2.26 (m, 2H, $-CH_2-$), 1.55 (m, 2H, $-CH_2-$), 1.48 (m, 2H, $-CH_2-$), 1.39 (d, 18H, $J$ = 14.9, $PC(CH_3)_3$), 0.96 (t, 3H, $J$ = 7.5, $-CH_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 150.4 (d, $J$ = 15.2, quat), 142.4 (d, $J$ = 6.2, quat), 134.4 (d, $J$ = 1.1, Ar–CH), 133.0 (d, $J$ = 7.2, Ar–CH), 130.1 (d, $J$ = 2.1, Ar–CH), 129.2 (s, Ar–CH), 128.9 (s, Ar–CH), 128.0 (s, Ar–CH), 127.7 (d, $J$ = 38.8, quat), 126.5 (d, $J$ = 6.2, Ar–CH), 120.4 (d, $J$ = 131.8, ≡C–), 103.0 (d, $J$ = 23.5, ≡C–), 37.4 (d, $J$ = 22.5, $PC(CH_3)_3$), 32.4 (s, $-CH_2-$), 31.0 (d, $J$ = 7.2, $PC(CH_3)_3$), 22.3 (s, $-CH_2-$), 19.9 (d, $J$ = 2.3, $-CH_2-$), 13.9 (s, $-CH_3$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 64.4 (s).

**Preparation of 15.** The general procedure was followed with (JohnPhos)AuCl (0.20 g, 0.377 mmol), ethynylferrocene (0.08 g, 0.381 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–60 : 40) to afford 0.23 g (86.7%) of an orange powder. Anal. Calcd for $C_{32}H_{36}AuFeP$: C, 54.56; H, 5.15. Found: C, 54.74; H, 4.99. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 7.85 (m, 1H, Ar–H), 7.58 (m, 1H, Ar–H), 7.51–7.42 (m, 4H, Ar–H), 7.27 (m, 1H, Ar–H), 7.18 (m, 2H, Ar–H), 4.37 (m, 2H, Ar–H), 4.22 (s, 5H, Ar–H), 4.06 (m, 2H, Ar–H), 1.41 (d, 18H, $J$ = 14.9, $PC(CH_3)_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 150.3 (d, $J$ = 15.7, quat), 142.4 (d, $J$ = 6.2, quat), 134.4 (s, Ar–CH), 133.1 (d, $J$ = 7.2, Ar–CH), 130.1 (d, $J$ = 3.2, Ar–CH), 130.1 (d, $J$ = 132.4, ≡C–), 129.3 (s, Ar–CH), 129.0 (s, Ar–CH), 128.0 (s, Ar–CH), 127.7 (d, $J$ = 39.2, quat), 126.5 (d, $J$ = 5.6, Ar–CH), 99.2 (d, $J$ = 23.5, ≡C–), 71.6 (s, ═CH), 69.8 (s, ═CH), 69.5 (d, $J$ = 2.9, quat), 67.3 (s, ═CH), 37.4 (d, $J$ = 22.3, $PC(CH_3)_3$), 31.1 (d, $J$ = 7.2, $PC(CH_3)_3$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 25 °C): $\delta$ 64.5 (s).

**Preparation of 16.** The general procedure was followed with (JohnPhos)AuCl (0.20 g, 0.377 mmol), 2-methyl-3-butyn-2-ol (36.8 µl, 0.380 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–60 : 40) to afford 0.19 g (87.2%) of a white powder. Anal. Calcd for $C_{25}H_{34}AuOP$: C, 51.91; H, 5.92. Found: C, 51.65; H, 6.12. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 7.85 (t, 1H, $J$ = 7.8, Ar–H), 7.51–7.44 (m, 5H, Ar–H),

7.26 (m, 1H, Ar–H), 7.15 (m, 2H, Ar–H), 1.96 (s, 1H, OH), 1.56 (s, 6H, $-CH_3$), 1.39 (d, 18H, $J$ = 15.0, $-CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 150.3 (d, $J$ = 15.2, quat), 142.5 (d, $J$ = 6.2, quat), 134.3 (d, $J$ = 1.1, Ar–H), 133.1 (d, $J$ = 7.2, Ar–H), 130.2 (d, $J$ = 2.3, Ar–H), 129.2 (s, Ar–H), 128.9 (s, Ar–H), 127.9 (s, Ar–H), 127.6 (d, $J$ = 39.8, quat), 126.6 (d, $J$ = 5.6, Ar–H), 123.1 (d, $J$ = 131.4, ≡C–), 107.0 (d, $J$ = 22.5, ≡C–), 65.5 (d, $J$ = 1.7, quat), 37.4 (d, $J$ = 22.5, P$C$($CH_3$)$_3$), 32.7 (s, $-CH_3$), 31.0 (d, $J$ = 6.6, PC($CH_3$)$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 64.5 (s).

**Preparation of 17.** The general procedure was followed with (JohnPhos)AuCl (0.20 g, 0.377 mmol), propargyl alcohol (22.0 µL, 0.380 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–60 : 40) to afford 0.13 g (62.7%) of a white powder. Anal. Calcd for $C_{23}H_{30}AuOP$: C, 50.19; H, 5.49. Found: C, 49.80; H, 5.72. $^1H$ NMR ($CDCl_3$, 25 °C): $\delta$ 7.85 (m, 1H, Ar–H), 7.51–7.40 (m, 5H, Ar–H), 7.28 (m, 1H, Ar–H), 7.15 (m, 2H, Ar–H), 4.31 (dd, 2H, $J$ = 6.0, 1.2, C(OH)$H_2$), 1.40 (d, 18H, $J$ = 15.0, PC(C$H_3$)$_3$), 1.36 (t, 1H, $J$ = 6.0, C(O$H$)H$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 150.2 (d, $J$ = 15.1, quat), 142.5 (d, $J$ = 6.2, quat), 134.3 (d, $J$ = 1.2, Ar–CH), 133.1 (d, $J$ = 7.2, Ar–CH), 130.3 (d, $J$ = 2.3, Ar–CH), 129.2 (s, Ar–CH), 128.9 (s, Ar–CH), 128.1 (d, $J$ = 130.1, ≡C–), 127.9 (s, Ar–CH), 127.4 (d, $J$ = 39.8, quat), 126.6 (d, $J$ = 5.7, Ar–CH), 100.5 (d, $J$ = 22.9, ≡C–), 52.2 (d, $J$ = 2.3, $C$(OH)H$_2$), 37.5 (d, $J$ = 22.5, P$C$(CH$_3$)$_3$), 31.0 (d, $J$ = 6.6, PC($C$H$_3$)$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 64.1 (s).

**Preparation of 18.** The general procedure was followed with (tBuXPhos)AuCl (0.20 g, 0.304 mmol), phenylacetylene (33.5 µl, 0.305 mmol), NaOH (0.025 g, 0.625 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–60 : 40) to afford 0.16 g (72.7%) of a white powder. Anal. Calcd for $C_{37}H_{50}AuP$: C, 61.49; H, 6.97. Found: C, 61.36; H, 6.37. $^1H$ NMR ($CDCl_3$, 25 °C): $\delta$ 7.89 (m, 1H, Ar–CH), 7.45 (m, 2H, Ar–CH), 7.38 (m, 2H, Ar–CH), 7.31 (m, 1H, Ar–CH), 7.18 (m, 2H, Ar–CH), 7.11 (m, 3H, Ar–CH), 2.92 (sept, 1H, $J$ = 6.9, $^i$Pr–CH), 2.38 (sept, 2H, $J$ = 6.6, $^i$Pr–CH), 1.43 (d, 18H, $J$ = 15.0, PC(C$H_3$)$_3$), 1.36 (d, 6H, $J$ = 7.2, $^i$Pr–CH$_3$), 1.26 (d, 6H, $J$ = 7.2, $^i$Pr–CH$_3$), 0.93 (d, 6H, $J$ = 6.6, $^i$Pr–CH$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 149.4 (s, quat), 148.6 (d, $J$ = 15.7, quat), 145.6 (s, quat), 135.7 (d, $J$ = 2.0, quat), 135.5 (d, $J$ = 132.9, ≡C–), 135.3 (d, $J$ = 1.7, Ar–CH–), 134.7 (d, $J$ = 7.8, Ar–CH–), 132.2 (d, $J$ = 1.1, Ar–CH–), 129.7 (d, $J$ = 1.8, Ar–CH–), 129.5 (s, quat), 127.5 (s, Ar–CH–), 126.7 (d, $J$ = 2.3, quat), 126.1 (d, $J$ = 6.2, Ar–CH–), 125.5 (s, Ar–CH–), 121.9 (s, Ar–CH–), 101.6 (d, $J$ = 23.5, ≡C–), 38.1 (d, $J$ = 22.9, P$C$(CH$_3$)$_3$), 33.9 (s, $^i$PrCH–), 31.4 (d, $J$ = 6.6, PC($C$H$_3$)$_3$), 30.9 (s, $^i$PrCH–), 26.3 (s, $^i$Pr–CH$_3$), 24.0 (s, $^i$Pr–CH$_3$), 23.0 (s, $^i$Pr–CH$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 63.1 (s).

**Preparation of 19.** The general procedure was followed with (tBuXPhos)AuCl (0.20 g, 0.304 mmol), 1-hexyne (35.0 µl, 0.305 mmol), NaOH (0.025 g, 0.625 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–60 : 40) to afford 0.15 g (70.1%) of a white powder. Anal. Calcd for $C_{35}H_{54}AuP$: C, 59.82; H, 7.75. Found: C, 59.44; H, 8.01. $^1H$ NMR ($CDCl_3$, 25 °C): $\delta$ 7.86 (m, 1H, Ar–H), 7.42 (m, 2H, Ar–H), 7.27 (m, 1H, Ar–H), 7.07 (s, 2H, Ar–H), 2.97 (sept, 1H, $J$ = 6.9, $^i$Pr–CH), 2.34 (sept, 2H, $J$ = 6.9, $^i$Pr–CH), 2.17 (m, 2H, $-CH_2-$), 1.47 (m, 2H, $-CH_2-$), 1.38 (d, 18H, $J$ = 14.4, $-C(CH_3)_3$), 1.37 (m, 2H, $-CH_2-$), 1.36 (d, 6H, $J$ = 7.2, $^i$Pr–CH$_3$), 1.31 (d, 6H, $J$ = 7.2, $^i$Pr–CH$_3$), 0.90 (d, 6H, $J$ = 7.0, $^i$Pr–CH$_3$), 0.89 (t, 3H, $J$ = 7.2, $-CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 149.1 (s, quat), 148.5 (d, $J$ = 15.7, quat), 145.5 (s, quat), 135.7 (d, $J$ = 5.1, quat), 135.3 (d, $J$ = 1.7, =CH–), 134.7 (d, $J$ = 7.8, =CH–), 129.8 (d, $J$ = 35.9, quat), 129.6 (d, $J$ = 2.1, =CH–), 126.0 (d, $J$ = 5.6, =CH–), 121.8 (s, =CH–), 121.4 (d, $J$ = 133.5, ≡C–), 101.8 (d, $J$ = 24.1, ≡C–), 38.0 (d, $J$ = 23.1, P$C$(CH$_3$)$_3$), 34.0 (s, $^i$Pr–CH), 32.3 (s, $-CH_2-$), 31.4 (d, $J$ = 6.8, PC($C$H$_3$)$_3$), 30.8 (s, $^i$Pr–CH), 26.3 (s, $^i$Pr–CH$_3$), 24.0 (s, $^i$Pr–CH$_3$), 22.9 (s, $^i$Pr–CH$_3$), 22.3 (s, $-CH_2-$), 20.1 (d, $J$ = 2.3, $-CH_2-$), 13.8 (s, $-CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 64.1 (s).

**Preparation of 20.** The general procedure was followed with (tBuXPhos)AuCl (0.20 g, 0.304 mmol), ethynylferrocene (0.065 g, 0.309 mmol), NaOH (0.025 g, 0.625 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–60 : 40) to afford 0.22 g (87.0%) of an orange powder. Anal. Calcd for $C_{41}H_{54}AuFeP$: C, 59.28; H, 6.55. Found: C, 59.64; H, 6.36. $^1H$ NMR ($CDCl_3$, 25 °C): $\delta$ 7.89 (m, 1H, Ar–H), 7.49–7.42 (m, 2H, Ar–H), 7.29 (m, 1H, Ar–H), 7.13 (s, 2H, Ar–H), 4.31 (m, 2H, =CH), 4.18 (m, 5H, =CH), 4.03 (m, 2H, =CH), 3.08 (sept, 1H, $J$ = 6.8, $^i$PrCH), 2.38 (sept, 2H, $J$ = 6.8, $^i$PrCH), 1.43 (d, 6H, $J$ = 6.6, $^i$Pr–CH$_3$), 1.43 (d, 18H, $J$ = 15.0, PC(C$H_3$)$_3$), 1.37 (d, 6H, $J$ = 6.6, $^i$Pr–CH$_3$), 0.93 (d, 6H, $J$ = 6.6, $^i$Pr–CH$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 149.2 (s, quat), 148.5 (d, $J$ = 15.8, quat), 145.6 (s, quat), 135.7 (d, $J$ = 5.0, quat), 135.3 (d, $J$ = 1.1, Ar–CH), 134.7 (d, $J$ = 8.0, Ar–CH), 131.3 (d, $J$ = 134.1, ≡C–), 129.6 (d, $J$ = 36.5, quat), 129.6 (d, $J$ = 2.1, Ar–CH), 126.1 (d, $J$ = 5.7, Ar–CH), 121.9 (s, Ar–CH), 98.4 (d, $J$ = 24.6, ≡C–), 71.5 (s, =CH), 70.0 (d, $J$ = 2.9, quat), 69.8 (s, =CH), 67.1 (s, =CH), 38.1 (d, $J$ = 23.1, P$C$(CH$_3$)$_3$), 34.1 (s, $^i$PrCH), 31.5 (d, $J$ = 6.8, PC($C$H$_3$)$_3$), 30.9 (s, $^i$PrCH), 26.3 (s, $^i$Pr–CH$_3$), 24.4 (s, $^i$Pr–CH$_3$), 23.1 (s, $^i$Pr–CH$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 64.0 (s).

**Preparation of 21.** The general procedure was followed with (tBuXPhos)AuCl (0.20 g, 0.304 mmol), 1-ethynyl-1-cyclohexanol (0.038 g, 0.306 mmol), NaOH (0.025 g, 0.625 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–60 : 40) to afford 0.21 g (92.6%) of a white powder. Anal. Calcd for $C_{37}H_{56}AuOP$: C, 59.67; H, 7.58. Found: C, 59.40; H, 7.35. $^1H$ NMR ($CDCl_3$, 25 °C): $\delta$ 7.88 (m, 1H, Ar–H), 7.44 (m, 2H, Ar–H), 7.27 (m, 1H, Ar–H), 7.08 (s, 2H, Ar–H), 2.99 (sept, 1H, $J$ = 6.9, $^i$PrCH), 2.35 (sept, 2H, $J$ = 6.8, $^i$PrCH), 1.88 (s, 1H, –OH), 1.83 (m, 2H, $-CH_2-$), 1.64 (m, 4H, $-CH_2-$), 1.56 (m, 2H, $-CH_2-$), 1.46 (m, 1H, $-CH_2-$), 1.41 (d, 18H, $J$ = 14.7, PC(C$H_3$)$_3$), 1.37 (d, 6H, $J$ = 6.8, $^i$Pr–CH$_3$), 1.32 (d, 6H, $J$ = 6.8, $^i$Pr–CH$_3$), 1.27 (m, 1H, $-CH_2-$), 0.91 (d, 6H, $J$ = 6.5, $^i$Pr–CH$_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 149.1 (s, quat), 148.5 (d, $J$ = 15.7, quat), 145.6 (s, quat), 135.8 (d, $J$ = 5.1, quat), 135.3 (d, $J$ = 1.7, Ar–CH), 134.8 (d, $J$ = 7.8, Ar–CH), 129.7 (d, $J$ = 2.3, Ar–CH), 129.5, (d, $J$ = 36.5, quat), 126.2 (d, $J$ = 132.4, ≡C–), 126.1 (d, $J$ = 5.6, Ar–CH), 121.8 (s, Ar–CH), 105.4 (d, $J$ = 22.3, ≡C–), 68.9 (s, quat), 41.0 (s, $-CH_2-$), 38.1 (d, $J$ = 23.1, P$C$(CH$_3$)$_3$), 34.1 (s, $^i$Pr–CH), 31.4 (d, $J$ = 6.6, PC($C$H$_3$)$_3$), 30.9 (s, $^i$Pr–CH), 26.3 (s, $^i$Pr–CH$_3$), 25.7 (s, $-CH_2-$),

24.3 (s, $^{i}$Pr–$CH_3$), 23.6 (s, –$CH_2$–), 22.8 (s, $^{i}$Pr–$CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 64.9 (s)

**Preparation of 22.** The general procedure was followed with (SIMes)AuCl (0.20 g, 0.37 mmol), 1-hexyne (43 μL, 0.37 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–60 : 40) to afford 0.21 g (97.1%) of a white powder. Anal. Calcd for $C_{27}H_{35}AuN_2$: C, 55.48; H, 6.04. Found: C, 55.73; H, 6.27. $^1H$ NMR ($CDCl_3$, 25 °C): $\delta$ 6.92 (s, 4H, Ar–H), 3.90 (s, 4H, –$NCH_2CH_2N$–), 2.30 (s, 12H, –$CH_3$), 2.29 (s, 6H, –$CH_3$), 2.20 (t, 2H, $J$ = 7.5, –$CH_2$–), 1.40 (m, 2H, –$CH_2$–), 1.26 (m, 2H, –$CH_2$–), 0.79 (t, 3H, $J$ = 7.20, –$CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 210.4 (s, carbene C), 138.5 (s, quat), 135.6 (s, quat), 135.0 (s, quat), 129.7 (s, =CH–), 115.3 (s, ≡C–), 105.4 (s, ≡C–), 50.9 (s, –$NCH_2CH_2N$–), 32.5 (s, –$CH_2$–), 22.4 (s, –$CH_2$–), 21.1 (s, –$CH_3$), 20.0 (s, –$CH_2$–), 18.0 (s, –$CH_3$), 13.7 (s, –$CH_3$).

**Preparation of 23.** The general procedure was followed with (SIMes)AuCl (0.20 g, 0.37 mmol), ethynyl toluene (47.0 μL, 0.371 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–80 : 20) to afford 0.16 g (69.7%) of a white powder. Anal. Calcd for $C_{30}H_{33}AuN_2$: C, 58.25; H, 5.38. Found: C, 58.48; H, 5.72. $^1H$ NMR ($CDCl_3$, 25 °C): $\delta$ 7.20 (AA′BB′, 2H, Ar–H), 6.94 (s, 4H, Ar–H), 6.91 (AA′BB′, 2H, Ar–H), 3.93 (s, 4H, –$NCH_2CH_2N$–), 2.33 (s, 12H, –$CH_3$), 2.30 (s, 6H, –$CH_3$), 2.23 (s, 3H, –$CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 210.1 (s, carbene C), 138.6 (s, quat), 135.7 (s, quat), 135.6 (s, quat), 134.9 (s, quat), 132.1 (s, Ar–*C*H), 129.8 (s, Ar–*C*H), 128.4 (s, Ar–*C*H), 127.7 (s, quat or ≡C–), 122.5 (s, quat or ≡C–), 104.3 (s, ≡C–), 50.9 (s, –$NCH_2CH_2N$–), 21.3 (s, –$CH_3$), 21.1 (s, –$CH_3$), 18.1 (s, –$CH_3$).

**Preparation of 24.** The general procedure was followed with (SIMes)AuCl (0.20 g, 0.37 mmol), ethynylferrocene (0.078 g, 0.37 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). Recrystallization by diffusion of pentane into a saturated benzene/$CH_2Cl_2$ solution afforded 0.22 g (83.2%) of the title compound as orange needles. Anal. Calcd for $C_{33}H_{35}AuFeN_2$: C, 55.63; H, 4.95. Found: C, 55.99; H, 4.43. $^1H$ NMR ($CDCl_3$, 25 °C): $\delta$ 6.94 (s, 4H, Ar–CH), 4.20 (m, 2H, =CH), 4.09 (s, 5H, =CH), 3.97 (m, 2H, =CH), 3.91 (s, 4H, –$NCH_2CH_2N$–), 2.33 (s, 12H, –$CH_3$), 2.30 (s, 6H, –$CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 210.1 (s, carbene C), 138.5 (s, quat), 135.6 (s, quat), 135.0 (s, quat), 129.7 (s, Ar–CH), 125.0 (s, ≡C–), 101.4 (s, ≡C–), 71.6 (s, =CH), 69.7 (s, =CH), 68.9 (s, quat), 67.2 (s, =CH), 50.9 (s, –$NCH_2CH_2N$–), 21.1 (s, –$CH_3$), 18.1 (s, –$CH_3$).

**Preparation of 25.** The general procedure was followed with (SIMes)AuCl (0.20 g, 0.37 mmol), 1-ethynylcyclohexene (44.5 μL, 0.38 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–80 : 20) to afford 0.21 g (93.0%) of a white powder. Anal. Calcd for $C_{29}H_{35}AuN_2$: C, 57.23; H, 5.80. Found: C, 57.07; H, 5.62. $^1H$ NMR ($CDCl_3$, 25 °C): $\delta$ 6.91 (s, 4H, Ar–H), 5.87 (m, 1H, =CH), 3.90 (s, 4H, –$NCH_2CH_2N$–), 2.30 (s, 12H, –$CH_3$), 2.28 (s, 6H, –$CH_3$), 2.02 (m, 2H, –$CH_2$–), 1.96 (m, 2H, –$CH_2$–), 1.49 (m, 2H, –$CH_2$–), 1.45 (m, 2H, –$CH_2$–). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 210.3 (s, carbene C), 138.5 (s, quat), 135.6 (s, quat), 134.9 (s, quat), 132.0 (s, =*C*H), 129.7 (s, Ar–*C*H), 124.7 (s, quat), 121.8 (s, quat), 106.4 (s, ≡C–), 50.9 (s, N*C*$H_2$*C*$H_2$N–), 30.5 (s, –$CH_2$–), 25.6 (s, –$CH_2$–), 22.7 (s, –$CH_2$–), 21.8 (s, –$CH_2$–), 21.1 (s, –$CH_3$), 18.1 (s, –$CH_3$).

**Preparation of 26.** The general procedure was followed with (SIMes)AuCl (0.20 g, 0.37 mmol), 2-(3-butynyloxy)tetrahydro-2*H*-pyran (44.5 μL, 0.38 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–80 : 20) to afford 0.20 g (82.3%) of a white powder. Anal. Calcd for $C_{30}H_{39}AuN_2O_2$: C, 54.88; H, 5.99. Found: C, 54.69; H, 5.95. $^1H$ NMR ($CDCl_3$, 25 °C): $\delta$ 6.92 (s, 4H, Ar–H), 4.53 (m, 1H, –CH–), 3.90 (s, 4H, –$NCH_2CH_2N$–), 3.78 (m, 1H, –$CH_2$–), 3.70 (m, 1H, –$CH_2$–), 3.47 (m, 1H, –$CH_2$–), 3.38 (m, 1H, –$CH_2$–), 2.53 (m, 2H, –$CH_2$–), 2.30 (s, 12H, –$CH_3$), 2.29 (s, 6H, –$CH_3$), 1.76 (m, 1H, –$CH_2$–), 1.62 (m, 1H, –$CH_2$–), 1.50 (m, 2H, –$CH_2$–), 1.44 (m, 2H, –$CH_2$–), $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 210.2 (s, carbene C), 138.5 (s, quat), 135.6 (s, quat), 134.9 (s, quat), 129.7 (s, Ar–*C*H), 117.3 (s, quat), 100.6 (s, ≡C–), 98.5 (s, –CH–), 67.1 (s, –$CH_2$–), 62.0 (s, –$CH_2$–), 50.9 (s, –N*C*$H_2$*C*$H_2$N–), 30.6 (s, –$CH_2$–), 25.4 (s, –$CH_2$–), 21.5 (s, –$CH_2$–), 21.1 (s, –$CH_3$), 19.5 (s, –$CH_2$–), 18.0 (s, –$CH_3$).

**Preparation of 27.** The general procedure was followed with (SIMes)AuCl (0.20 g, 0.37 mmol), methyl propiolate (33.0 μL, 0.37 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). The title compound was purified by column chromatography (THF/hexane gradient 10 : 90–80 : 20) to afford 0.15 g (68.9%) of a white powder. Anal. Calcd for $C_{25}H_{29}AuN_2O_2$: C, 51.20; H, 4.98. Found: C, 50.91; H, 4.75. $^1H$ NMR ($CDCl_3$, 25 °C): $\delta$ 6.94 (s, 4H, Ar–H), 3.96 (s, 4H, –$NCH_2CH_2N$–), 3.59 (s, 3H, –$OCH_3$), 2.30 (s, 6H, –$CH_3$), 2.29 (s, 12H, –$CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 209.0 (s, carbene C), 153.9 (s, C=O), 138.9 (s, quat), 135.5 (s, quat), 134.5 (s, quat), 133.3 (s, quat), 129.8 (s, Ar–CH), 93.5 (s, ≡C–), 51.8 (s, –$OCH_3$), 51.0 (s, –$NCH_2CH_2N$–), 21.1 (s, –$CH_3$), 18.0 (s, –$CH_3$).

**Preparation of 28.** The general procedure was followed with (SIMes)AuCl (0.20 g, 0.37 mmol), ethisterone (0.12 g, 0.38 mmol; dissolved in 10 mL methanol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). Recrystallization by diffusion of pentane into a saturated benzene solution afforded 0.25 g (82.7%) of the title compound as white needles. Anal. Calcd for $C_{42}H_{53}AuN_2O_2$: C, 61.91; H, 6.56. Found: C, 62.03; H, 6.27. $^1H$ NMR ($CDCl_3$, 25 °C): $\delta$ 6.93 (s, 2H, Ar–H), 6.92 (s, 2H, Ar–H), 5.73 (s, 1H, =CH), 3.91(s, 4H, –$NCH_2CH_2N$–), 2.47–2.20 (m, 4H, –$CH_2$–), 2.31 (s, 12H, –$CH_3$), 2.28 (s, 6H, –$CH_3$), 2.13 (m, 1H, –$CH_2$–), 2.05 (m, 1H, –$CH_2$–), 1.89 (m, 1H, –$CH_2$–), 1.78–1.67 (m, 3H, –$CH_2$–), 1.62–1.53 (m, 2H, –$CH_2$–), 1.47–1.41 (m, 3H, –$CH_2$– and –CH–), 1.34 (m, 1H, –$CH_2$–), 1.17 (m, 1H, –$CH_2$–), 1.17 (s, 3H, –$CH_3$), 0.97 (m, 1H, –$CH_2$–), 0.88 (m, 1H, –CH–), 0.77 (s, 3H, –$CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 210.2 (s, carbene C), 199.7 (s, quat), 172.1 (s, quat), 138.5 (s, quat), 135.6 (s, quat), 134.9 (s, quat), 129.61 (s, Ar–CH), 129.58 (s, Ar–CH), 123.6 (s, =CH), 122.3 (s, ≡C–), 107.5 (s, ≡C–), 80.1 (s, quat), 53.4 (s, –CH–), 50.9 (s, –$NCH_2CH_2N$–), 49.2 (s, –CH–), 46.4 (s, quat), 39.6 (s, –$CH_2$–), 38.7 (s, quat), 36.3 (s, –CH–), 35.8 (s, –$CH_2$–), 34.1 (s, –$CH_2$–), 33.0 (s, –$CH_2$–), 32.5 (s, –$CH_2$–), 31.5 (s, –$CH_2$–), 23.1 (s, –$CH_2$–), 21.1 (s, –$CH_3$), 20.9 (s, –$CH_2$–), 18.1 (s, –$CH_3$), 17.4 (s, –$CH_3$), 12.9 (s, –$CH_3$).

**Preparation of 29.** The general procedure was followed with (SIMes)AuCl (0.20 g, 0.37 mmol), 1-ethynyl-1-cyclohexanol (0.046 g, 0.37 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). Recrystallization by diffusion of pentane into a saturated benzene solution afforded 0.18 g (77.4%) of the title compound as a white powder. Anal. Calcd for $C_{29}H_{37}AuN_2O$: C, 55.59; H, 5.95. Found: C, 55.50; H, 5.79. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 6.94 (s, 4H, Ar–CH), 3.90 (s, 4H, –$NCH_2CH_2N$–), 2.31 (br s, 18H, –$CH_3$), 1.78 (s, 1H, –OH), 1.71 (m, 2H, –$CH_2$), 1.51 (m, 6H, –$CH_2$), 1.27 (m, 2H, –$CH_2$–). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 210.2 (s, carbene C), 138.5 (s, quat), 135.6 (s, quat), 134.9 (s, quat), 129.7 (s, Ar–CH), 119.4 (s, ≡C–), 108.6 (s, ≡C–), 68.4 (s, quat), 50.9 (s, –$NCH_2CH_2N$–), 40.7 (s, –$CH_2$–), 25.5 (s, –$CH_2$–), 23.0 (s, –$CH_2$–), 21.1 (s, –$CH_3$), 18.1 (s, –$CH_3$).

**Preparation of 30.** The general procedure was followed with (SIMes)AuCl (0.20 g, 0.37 mmol), 2-methyl-3-butyn-2-ol (36 µL, 0.37 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). Recrystallization by diffusion of pentane into a saturated benzene solution afforded 0.16 g (73.5%) of the title compound as a white powder. Anal. Calcd for $C_{26}H_{33}AuN_2O$: C, 53.24; H, 5.67. Found: C, 53.20; H, 5.29. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 6.94 (s, 4H, Ar–H), 3.90 (s, 4H, –$NCH_2CH_2N$–), 2.30 (s, 18H, –$CH_3$), 1.41 (s, 6H, –$CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 210.0 (s, carbene C), 138.5 (s, quat), 135.6 (s, quat), 134.9 (s, quat), 129.7 (s, Ar–*C*H), 118.0 (s, ≡C–), 109.1 (s, ≡C–), 65.5 (s, quat), 50.9 (s, –$NCH_2CH_2N$–), 32.6 (s, –$CH_3$), 21.1 (s, –$CH_3$), 18.1 (s, –$CH_3$).

**Preparation of 31.** The general procedure was followed with (SIMes)AuCl (0.20 g, 0.37 mmol), propargyl alcohol (22 µL, 0.38 mmol), NaOH (0.030 g, 0.75 mmol), $CH_2Cl_2$ (5 mL), and MeOH (10 mL). Recrystallization by diffusion of pentane into a saturated benzene/$CH_2Cl_2$ solution of the title compound afforded 0.12 g (57.9%) white needles. Anal. Calcd for $C_{24}H_{29}AuN_2O$: C, 51.62; H, 5.23. Found: C, 51.85; H, 5.85. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 6.93 (s, 4H, Ar–H), 4.24 (d, 2H, $J$ = 6.6, –$CH_2$–), 3.93 (s, 4H, –$NCH_2CH_2N$–), 2.31 (s, 12H, –$CH_3$), 2.29 (s, 6H, –$CH_3$), 1.32 (t, 1H, $J$ = 6.0, –OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 209.8 (carbene C), 138.7 (s, quat), 135.5 (s, quat), 134.7 (s, quat), 129.6 (s, Ar–CH), 123.0 (s, ≡C–), 102.6 (s, ≡C–), 52.1 (s, –$OCH_2$–), 50.9 (s, –$NCH_2CH_2N$–), 21.1 (s, –$CH_3$), 18.0 (s, –$CH_3$).

**Preparation of $Ph_3PAu(P(O)(OEt)_2)$.** An NMR tube was charged with 0.040 mmol of the alkynylgold complex (**1–12**) along with diethylphosphite (5.15 µL, 0.040 mmol), and $C_6D_6$ (0.5 mL). The NMR tubes were sealed in air and immersed in an oil bath at 64 °C. The reactions were monitored by NMR spectroscopy until the starting alkynylgold complex was consumed (>95%). After the alkynylgold complex was consumed, an internal standard (anisole or hexamethylbenzene) was added to the reaction mixture. Comparison of the resonances for the internal standard with the title compound provided the NMR conversions. The reaction mixture was concentrated under vacuum, triturated with a 2 : 1 mixture of diethylether : hexane, and dried under vacuum to afford the gold phosphonate as a white solid. Unless specified, the isolated yields obtained for each alkynylgold precursor are listed in Tables 2 and 5. Anal. Calcd for $C_{22}H_{25}AuO_3P$: C, 44.31; H, 4.23. Found: C, 44.21; H, 4.27. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 7.55–7.46 (m, 15H, –$C_6H_5$), 4.09 (m, 4H, –$OCH_2CH_3$), 1.34 (t, 6H, $J$ = 7.2, –$CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 134.2 (d, $J$ = 14.0, –$C_6H_5$), 131.8 (d, $J$ = 2.3, –$C_6H_5$), 129.4 (d, $J$ = 11.3, –$C_6H_5$), 129.2 (d, $J$ = 52.2, –$C_6H_5$), 57.8 (d, $J$ = 3.3, –$OCH_2CH_3$), 17.0 (d, $J$ = 6.6, –$OCH_2CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 110.3 (d, $J$ = 521.4 Hz, $P$(O)$(OEt)_2$), 44.6 (d, $J$ = 522.3, $PPh_3$).

**Preparation of (JohnPhos)Au(P(O)(OEt)$_2$).** An NMR tube was charged with 0.040 mmol of the alkynylgold complex (**13–17**) along with diethylphosphite (5.15 µL, 0.040 mmol), and $C_6D_6$ (0.5 mL). The NMR tubes were sealed in air and immersed in an oil bath at 64 °C. The reactions were monitored by NMR spectroscopy until the starting alkynylgold complex was consumed (>95%). After the alkynylgold complex was consumed, an internal standard (anisole or hexamethylbenzene) was added to the reaction mixture. Comparison of the resonances for the internal standard with the title compound provided the NMR conversions. The reaction mixture was concentrated under vacuum, triturated with hexane, and dried under vacuum to afford the gold phosphonate as a white solid. Unless specified, the NMR and isolated yields obtained for each alkynylgold precursor are listed in Tables 3 and 5. Anal. Calcd for $C_{24}H_{37}AuO_3P_2$: C, 45.58; H, 5.90. Found: C, 45.20; H, 6.12. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 7.85 (m, 1H, Ar–H), 7.57 (m, 2H, Ar–H), 7.49 (m, 3H, Ar–H), 7.26 (m, 1H, Ar–H), 7.18 (m, 2H, Ar–H), 3.84 (m, 4H, –$OCH_2CH_3$), 1.41 (d, 18H, $J$ = 15.0, PC($CH_3$)$_3$), 1.25 (t, 6H, $J$ = 7.2, –$OCH_2CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 150.2 (d, $J$ = 16.1, quat), 141.2 (d, $J$ = 6.8, quat), 134.7 (d, $J$ = 6.8,Ar–CH), 132.9 (d, $J$ = 7.4, Ar–CH), 130.6 (d, $J$ = 1.8, Ar–CH), 129.5 (s, Ar–CH), 128.8 (s, Ar–CH), 128.6 (s, Ar–CH), 126.8 (dd, $J$ = 34.8, 6.2, quat), 126.8 (dd, $J$ = 5.3, 1.4, Ar–CH), 56.9 (d, $J$ = 2.3, –$OCH_2CH_3$), 37.8 (d, 18.5, P$C(CH_3)_3$)), 31.0 (dd, $J$ = 6.8, 1.1, PC($CH_3$)$_3$), 16.9 (d, $J$ = 6.6, –$OCH_2CH_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 111.4 (d, $J$ = 473.2, –$P$(O)$(OEt)_2$), 65.6 (d, $J$ = 473.0, $P^tBu_2$).

**Preparation of (tBuXPhos)Au(P(O)(OEt)$_2$).** An NMR tube was charged with 0.040 mmol of the alkynylgold complex (**18–21**) along with diethylphosphite (5.15 µL, 0.040 mmol), and $C_6D_6$ (0.5 mL). The NMR tubes were sealed in air and immersed in an oil bath at 64 °C. The reactions were monitored by NMR spectroscopy until the starting alkynylgold complex was consumed (>95%). After the alkynylgold complex was consumed, an internal standard (anisole or hexamethylbenzene) was added to the reaction mixture. Comparison of the resonances for the internal standard with the title compound provided the NMR conversions. The reaction mixture was concentrated under vacuum, triturated with hexane, and dried under vacuum to afford the gold phosphonate as a white solid. Unless specified, the NMR and isolated yields obtained for each alkynylgold precursor are listed in Tables 3 and 5. Anal. Calcd for $C_{33}H_{55}AuO_3P_2$: C, 52.24; H, 7.31. Found: C, 52.01; H, 7.45. $^1$H NMR ($CDCl_3$, 25 °C): $\delta$ 7.87 (m, 1H, Ar–H), 7.46 (m, 2H, Ar–H), 7.26 (m, 1H, Ar–H), 7.17 (m, 2H, Ar–H), 3.77 (m, 4H, –$CH_2$–), 3.04 (sept, 1H, $J$ = 6.9, $^i$PrCH), 2.36 (sept, 2H, $J$ = 6.6, $^i$PrCH), 1.43 (d, 18H, $J$ = 14.4, PC($CH_3$)$_3$), 1.35 (d, 6H, $J$ = 6.6, $^i$Pr–$CH_3$), 1.32 (d, 6H, $J$ = 6.6, $^i$Pr–$CH_3$), 1.20 (t, 6H, $J$ = 7.2, –$CH_2CH_3$), 0.91 (d, 6H, $J$ = 6.0, $^i$Pr–$CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 149.1 (s, quat), 148.3 (d, $J$ = 16.9, quat), 145.4 (s, quat), 135.6 (d, $J$ = 6.6, Ar–CH), 135.2 (d, $J$ = 5.0, quat), 134.7 (d, $J$ = 8.4, Ar–CH), 130.1 (d, $J$ = 2.3, Ar–CH), 129.1 (dd, $J$ = 32.2, 6.4, quat), 126.4 (dd, $J$ = 3.9, 1.7, Ar–CH), 122.4 (s, Ar–CH), 56.6 (d, $J$ = 2.3, –$OCH_2CH_3$), 38.4 (d, $J$ = 19.0, quat), 33.4 (s, $^i$PrCH), 31.4 (d, $J$ = 6.6, PC($CH_3$)$_3$), 31.0

(s, $^{i}$PrCH), 26.4 (s, $^{i}$Pr–$CH_3$), 23.6 (s, $^{i}$Pr–$CH_3$), 23.0 (s, $^{i}$Pr–$CH_3$), 16.8 (d, $J$ = 7.2, –$OCH_2CH_3$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 112.7 (d, $J$ = 479.3, $P$(O)$(OEt)_2$), 65.5 (d, $J$ = 479.0, $P^{t}Bu_2$).

**Preparation of (SIMes)Au(P(O)(OEt)$_2$).** An NMR tube was charged with 0.040 mmol of the alkynylgold complex (**22–31**) diethylphosphite (5.15 μL, 0.040 mmol), and $C_6D_6$ (0.5 mL). The NMR tubes were sealed in air and immersed in an oil bath at 64 °C. The reactions were monitored by NMR spectroscopy until the starting alkynylgold complex was consumed (>95%). As the title compound is insoluble in $C_6D_6$, it was separated from the reaction mixture by centrifugation and triturated with fresh benzene (0.5 mL) to afford a white solid (dried under vacuum). Unless specified, the isolated yields obtained for each alkynylgold precursor are listed in Tables 4 and 5. Anal. Calcd for $C_{25}H_{36}AuN_2O_3P$: C, 46.88; H, 5.67. Found: C, 46.63; H, 5.86. $^{1}H$ NMR ($CDCl_3$, 25 °C): $\delta$ 6.94 (s, 4H, Ar–H), 4.00 (s, 4H, –$NCH_2$–), 3.55 (m, 4H, –$OCH_2$–), 2.32 (s, 12H, Ar–C$H_3$), 2.29 (s, 6H, Ar–C$H_3$), 0.99 (t, 6H, $J$ = 7.0, –$CH_2CH_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 216.2 (d, $J$ = 170.0, carbene C), 139.0 (s, quat), 135.6 (s, quat), 134.3 (s, quat), 129.7 (s, Ar–CH), 57.2 (s, –N$CH_2$–), 51.1 (d, $J$ = 6.2, O$CH_2$CH$_3$), 21.0 (s, Ar–$CH_3$), 18.0 (s, Ar–$CH_3$), 16.7 (d, $J$ = 6.6, OCH$_2$$CH_3$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 112.2 (s).

**Preparation of (JohnPhos)Au(P(O)($O_2C_2Me_4$)).** An NMR tube was charged with 0.040 mmol of **13** along with HP(O)($O_2C_2Me_4$) (0.0066 g, 0.040 mmol), and $C_6D_6$ (0.5 mL). The NMR tube was sealed in air and immersed in an oil bath at 64 °C. After 14 h, the reaction mixture was concentrated under vacuum, triturated with hexane, and dried under vacuum. Purification of residue by column chromatography (Silica gel : THF/MeOH gradient 100 : 0–50 : 50) afforded the gold phosphonate as a viscous oil (0.022 g, 84%). Anal. Calcd for $C_{26}H_{39}AuO_3P_2$: C, 47.42; H, 5.97. Found: C, 47.08; H, 6.51. $^{1}H$ NMR ($CDCl_3$, 25 °C): $\delta$ 7.85 (m, 1H, Ar–H), 7.57 (m, 3H, Ar–H), 7.49 (m, 2H, Ar–H), 7.27 (m, 1H, Ar–H), 7.16 (m, 2H, Ar–H), 1.40 (d, 18H, $J$ = 15.6, C($CH_3$)$_3$), 1.37 (s, 6H, –$CH_3$), 1.20 (s, 6H, –$CH_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 150.2 (d, $J$ = 16.0, quat), 141.0 (d, $J$ = 6.5, quat), 134.5(d, $J$ = 6.8, Ar–CH), 132.8 (d, $J$ = 7.4, Ar–CH), 130.5 (d, $J$ = 2.3, Ar–CH), 129.6 (s, Ar–CH), 129.5 (s, Ar–CH), 128.6 (s, Ar–CH), 126.7 (dd, $J$ = 35.0, 6.5, quat), 126.8 (dd, $J$ = 5.7, 1.5, Ar–CH), 83.5 (d, $J$ = 4.9, –O$C_2$Me$_4$), 37.5 (dd, $J$ = 18.3, 1.3, –$C$($CH_3$)$_3$), 31.0 (dd, $J$ = 6.8, 1.6, –C($CH_3$)$_3$), 25.2 (d, $J$ = 2.9, –$CH_3$), 25.1 (d, $J$ = 5.4, –$CH_3$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 120.2 (d, $J$ = 484.1, –P(O)($O_2C_2Me_4$), 65.0 (d, $J$ = 483.6, –P(C($CH_3$)$_3$)$_2$–).

**Preparation of (SIMes)Au(P(O)(OCH$_2$CMe$_2$CH$_2$O$^-$)).** An NMR tube was charged with 0.040 mmol of **29** along with HP(O)(OCH$_2$CMe$_2$CH$_2$O$^-$) (0.0060 g, 0.040 mmol), and $C_6D_6$ (0.5 mL). The NMR tube was sealed in air and immersed in an oil bath at 64 °C. After 14 h, the reaction mixture was concentrated under vacuum, triturated with hexane, and dried under vacuum. Purification of residue by column chromatography (Silica gel : THF/MeOH gradient 100 : 0–50 : 50) afforded the gold phosphonate as a white solid (0.020 g, 77%). Anal. Calcd for $C_{26}H_{36}AuN_2O_3P$: C, 47.86; H, 5.56. Found: C, 47.51; H, 5.93. $^{1}H$ NMR ($CDCl_3$, 25 °C): $\delta$ 6.96 (s, 4H, Ar–H), 4.00 (s, 4H, –N$CH_2$–), 3.42 (m, 4H, –$OCH_2$–), 2.32 (s, 12H, –$CH_3$), 2.29 (s, 6H, –$CH_3$), 1.03 (s, 3H, –$CH_3$), 0.58 (s, 3H, –$CH_3$). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 215.8 (d, $J$ = 170.3, carbene C), 139.0 (s, quat), 135.0 (s, quat), 134.2 (s, quat), 129.8 (s, Ar–CH), 71.8 (d, $J$ = 1.7, –O$CH_2$–), 51.2 (d, $J$ = 5.6, –N$CH_2$–), 31.8 (d, $J$ = 5.3, quat), 22.7 (s, –$CH_3$), 21.04 (s, –$CH_3$), 21.00 (s, –$CH_3$), 18.0 (s, –$CH_3$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 25 °C): $\delta$ 110.9 (s).

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