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Exploring the Influence of Phosphine Ligation on the Gold-Catalyzed Hydrohydrazination of Terminal Alkynes at Room Temperature

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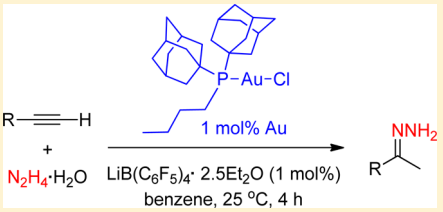
Supporting Information

ABSTRACT: The synthesis and/or NMR/X-ray characterization of a new series of (L)AuCl complexes is reported, featuring BippyPhos, AdJohnPhos, silyl ether based ligands including OTips-DalPhos, and PAd-DalPhos. These complexes, along with previously reported analogues featuring cataCXium-A, *t*BuJohnPhos, and Mor-DalPhos, were screened as precatalysts using $LiB(C_6F_5)_4 \cdot 2.5Et_2O$ as an activator in the hydrohydrazination of terminal aryl alkynes with hydrazine hydrate under unprecedentedly mild conditions (25 °C, 1 mol % Au). The precatalyst (cataCXium-A)AuCl proved to be particularly effective in such transformations, demonstrating useful scope.

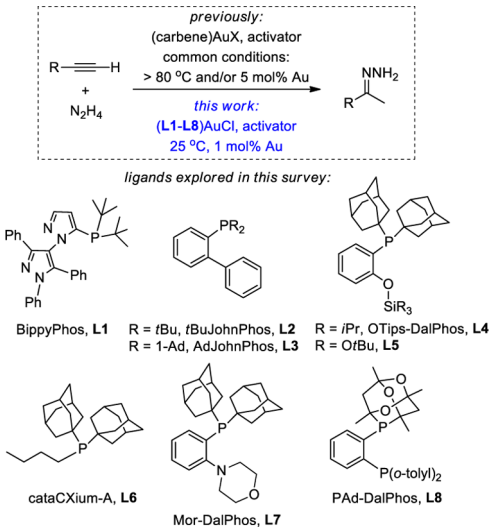


INTRODUCTION

Hydroamination and related additions of N−H bonds across unsaturated substrates represents an attractive means of preparing sought-after organic nitrogen compounds in an atom-economical fashion.[1] Given the particularly high activation barrier associated with the direct addition of N−H bonds to unactivated carbon−carbon multiple bonds of alkenes and alkynes,[2] the development of catalysts for such transformations has emerged as an important goal in modern synthetic chemistry. As a result, a diversity of hydroamination catalyst classes, most notably organometallic variants, have emerged over the past 20 years, enabling transformations of a broad spectrum of substrates.[1] Notwithstanding such progress, hydrohydrazination reactions involving parent hydrazine, a cheap and readily available reagent that is prepared and used on an industrial scale,[3] remain relatively unexplored. A number of challenges associated with using hydrazine in this and other metal-catalyzed transformations exist, including unwanted metal reduction[4] leading to potentially inactive aggregates.

Whereas hydrohydrazinations involving hydrazine/hydrazide derivatives, including in the absence of a metal catalyst,[5] have been demonstrated in a variety of contexts,[6] the first transformation of this type using parent hydrazine was reported only recently (Scheme 1). In their pioneering 2011 report, Bertrand and co-workers[7] employed a bulky cyclic (alkyl)-aminocarbene-ligated Au(I) precatalyst in the hydrohydrazination of alkynes and allenes (typically ≥90 °C, 5 mol % Au). Whereas these workers later established the utility of anti-Bredt N-heterocyclic carbene (NHC) ligated Au(I) precatalysts in room-temperature hydrohydrazinations of terminal alkyl-substituted alkynes (5 mol % Au),[8] efforts to extend this room-temperature catalysis to terminal aryl alkynes were unsuccessful. Notably, this substrate limitation was overcome by Hashmi and co-workers[9] in 2014. In employing appropriately substituted saturated abnormal NHCs, these workers achieved the first and only room-temperature hydrohydrazinations of terminal aryl alkynes (5 mol % Au) and did so using the more convenient reagent hydrazine hydrate,[9] rather than anhydrous hydrazine.[7,8,10] A 2017 report by Mendoza-Espinosa and co-workers[11] focusing on mesoionic carbene ligation revealed that Au(I) precatalysts outperform Au(III) species in the hydrohydrazination of terminal aryl alkynes (80 °C, 3 mol % Au).[10] Computational analyses by Ujaque, Lledós, and co-

Scheme 1. Gold-Catalyzed Hydrohydrazination of Terminal Alkynes with Hydrazine (X = Halide)



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workers[12] support a reaction pathway involving alkyne activation by cationic (carbene)Au^{I} species in alkyne hydrohydrazination chemistry employing parent hydrazine, thereby reaffirming the importance of employing a halide abstraction agent as a means of activating a neutral LAuX precatalyst (X = halide).

Collectively, the aforementioned reports would appear to suggest that carbene-based ancillary ligation is a prerequisite for Au-catalyzed alkyne hydrohydrazination with hydrazine, especially considering the poor performance of PPh_3AuCl in this chemistry.[9] In combining our interests in ancillary ligand design for Au-catalyzed alkyne hydroamination[13] and in developing synthetically useful transformations of parent hydrazine,[14] we sought to test this idea by exploring the feasibility of employing phosphines in Au-catalyzed alkyne hydrohydrazination with hydrazine, with the goal of expanding our appreciation of the ancillary ligand structures that give rise to efficient catalysts (Scheme 1). Herein we report the results of our investigation, which establish (**L6**)AuCl (**L6** = cataCXium-A) as a state of the art precatalyst for such hydrohydrazinations of terminal aryl alkynes (typically 25 °C, 1 mol % Au, using hydrazine hydrate).

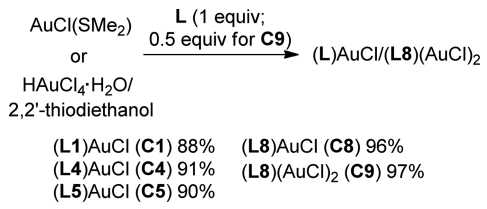
RESULTS AND DISCUSSION

In selecting phosphines to employ in our survey, we envisioned that sterically demanding ligands might work best in supporting reactive, low-coordinate, cationic Au(I) centers, in part by discouraging bimolecular decomposition. With this in mind, the following ligands were chosen (Scheme 1): BippyPhos (**L1**); *t*BuJohnPhos (**L2**); AdJohnPhos (**L3**); OTips-DalPhos (**L4**) and the new variant **L5**; cataCXium-A (**L6**); Mor-DalPhos (**L7**); PAd-DalPhos (**L8**). This set of ligands was chosen intentionally to span monophosphines featuring or lacking a secondary donor moiety (i.e., (hetero)aryl, O, N), as well as a bisphosphine. From a practical perspective, **L1**−**L8** are all air-stable and, with the exception of **L5**, are commercially available.

Whereas (**L2**)AuCl (**C2**) and (**L7**)AuCl (**C7**) were obtained from commercial sources, and (**L3**)AuCl (**C3**)[13] and (**L6**)AuCl (**C6**)[15] were prepared using literature methods, the otherwise new (**L**)AuCl complexes derived from **L1** (**C1**), **L4** (**C4**), **L5** (**C5**), and **L8** (**C8**) were prepared in high yield either by displacement of dimethyl sulfide from $AuCl(SMe_2)$ or from $HAuCl_4{\cdot}H_2O$ under reducing conditions (Scheme 2, see the Experimental Section). The presence of two phosphorus atoms in **L8** was exploited in the preparation of the digold species $(\mathbf{L8})(AuCl)_2$ (**C9**).

Each of the new complexes reported herein was identified on the basis of NMR and elemental analysis data, as well as single-crystal X-ray diffraction data (Figure 1); X-ray data for **C3** are also provided. The metrical parameters found within the solid-state structures of these complexes (Table S1 in the Supporting Information) neither are unusual nor vary significantly, with Au−P (2.23−2.26 Å), Au−Cl (2.28−2.30 Å), and nearly linear P−Au−Cl linkages (170−179°) observed that are in agreement with previously reported compounds, including the cataCXium-A and Mor-DalPhos complexes **C6**[15] and **C7**[13] and (carbene)-AuCl complexes[8,10] that have been employed previously in alkyne hydrohydrazination employing hydrazine. The Au−Au distance (2.9700(3) Å) in **C9** is within the common range observed for aurophilic interactions.[16]

Scheme 2. Synthesis of Gold Precatalysts[a]



[a]Isolated percent yield of analytically pure material provided.

With a collection of phosphine-ligated Au(I) precatalysts in hand (i.e., **C1**−**C9**), we conducted a competitive screen involving the hydrohydrazination of phenylacetylene with hydrazine hydrate to give **1**, employing $LiB(C_6F_5)_4{\cdot}2.5Et_2O$ as a halide abstraction agent under mild conditions (4 h, 25 °C, 1 mol % precatalyst; Scheme 3). While most of the precatalysts surveyed afforded low consumption of the starting materials and ≤20% conversion to **1**, **C5** and **C6** both afforded high conversion to the target hydrazine product, with **C6** proving to be marginally superior. The success of **C5** and **C6** in enabling this reaction is noteworthy, given that Bertrand[8] and Hashmi[9] have each demonstrated the inability of otherwise effective (carbene)AuCl complexes to catalyze such a transformation under these mild conditions. Furthermore, the observation that the Mor-DalPhos ligated precatalyst **C7** is highly effective for the stereoselective hydroamination of internal aryl alkynes with dialkylamines[13] but is ineffective for the test transformation leading to **1** (Scheme 3) confirms that the ancillary ligand plays an important role in determining the successful outcome of Au-catalyzed hydroaminations in a substrate-dependent manner.

Having discovered that the cataCXium-A ligated complex **C6** is a capable precatalyst for the hydrohydrazination of phenylacetylene with hydrazine hydrate under mild conditions (4 h, 25 °C, 1 mol % Au), we then turned our attention to examining the scope of reactivity (Scheme 4). A range of substituted terminal aryl alkynes were accommodated successfully under these conditions; *p*-alkyl, -methoxy, and -halide substituents were well tolerated and the desired product in each case was generated in high yield (**2**−**6**, 87−98%). While the presence of an *o*-amino group within the phenylacetylene framework did somewhat inhibit conversion, the successful formation of **8** (52%) was nonetheless achieved at room temperature. Conversely, the *p*-trifluoromethyl-substituted phenylacetylene substrate leading to **7** proved to be particularly challenging, requiring more forcing conditions in order to achieve suitable conversion (94%; 14 h, 90 °C, 5 mol % Au), whereas by use of a saturated abnormal NHC ligand this transformation was enabled under more mild conditions (71%; 7 h, 20 °C, 5 mol % Au).[9] Attempts to employ 1-phenyl-2-trimethylsilylacetylene in place of phenylacetylene afforded high conversion (87%) to the desilylated product **1**. Suitably high conversion was also achieved when using 3-phenyl-1-propyne leading to **9** (70%), or terminal (hetero)aryl alkynes based on pyridine or thiophene, leading to **10** and **11** (98 and 75%, respectively). Although not explored broadly, the ability of the **C6**-based catalyst system to effect hydrohydrazinations of internal alkynes was established in the transformation of diphenylacetylene (14 h, 90 °C, 5 mol % Au), leading to **12** (83%).

CONCLUSIONS

In summary, the results of a screening process involving a crystallographically characterized series of phosphine-ligated and $LiB(C_6F_5)_4{\cdot}2.5Et_2O$-activated (**L**)AuCl precatalysts in the

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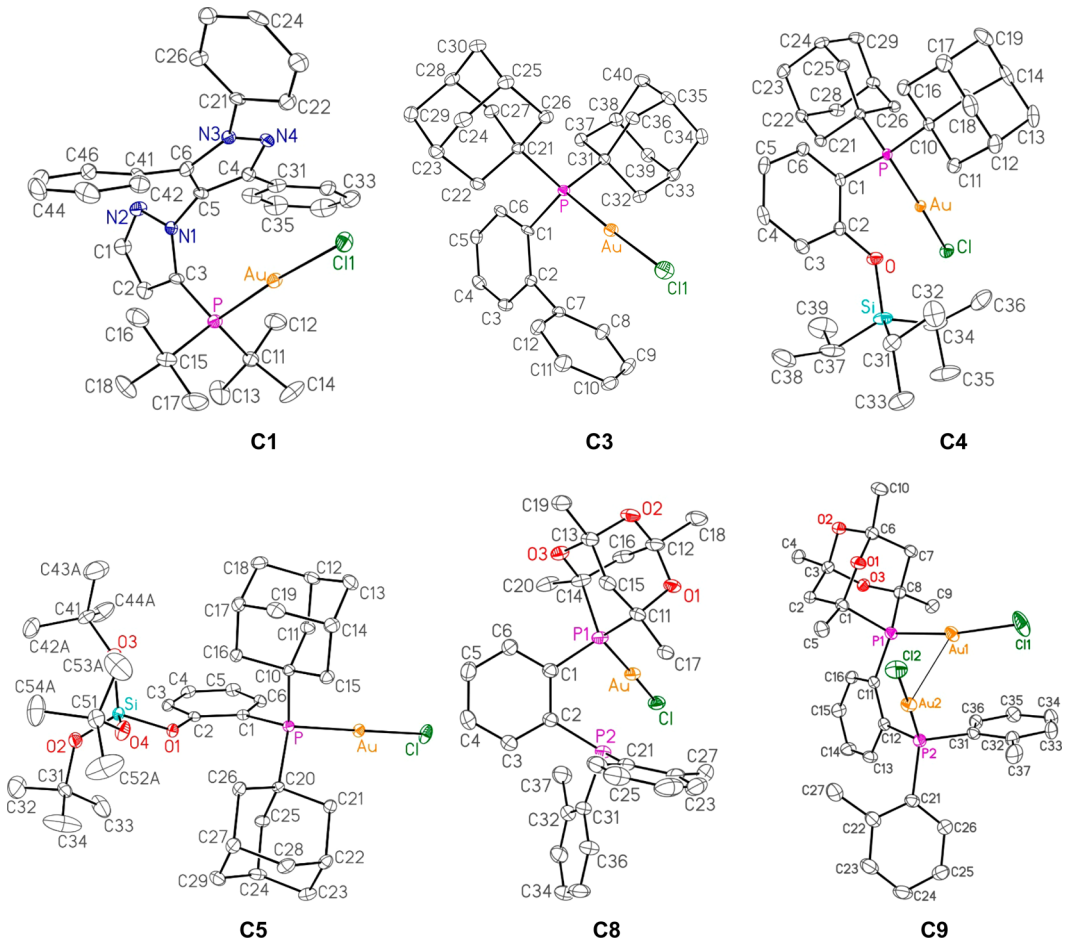
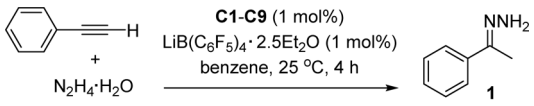


Figure 1. Single-crystal X-ray structures of some gold precatalyst complexes featured in this hydrohydrazination survey, shown with 30% thermal ellipsoids and with hydrogen atoms omitted for clarity.

Scheme 3. Phosphine Ligand Screen in the Room-Temperature, Gold-Catalyzed Hydrohydrazination of Phenylacetylene at Low Catalyst Loadings[a]



C1 <10% **C4** 20% **C7** <10%
C2 20% **C5** 90% **C8** <10%
C3 60% **C6** >95% (90%) **C9** <10%

[a]Estimated percent conversion to **1** stated on the basis of ^{1}H NMR data using trimethoxybenzene as an internal standard, and isolated percent yield given in parentheses.

hydrohydrazination of terminal aryl alkynes with hydrazine hydrate establish (**L6**)AuCl (**L6** = cataCXium-A) as being highly effective for these reactions. The ability of (**L6**)AuCl to effect such transformations under mild conditions (25 °C, 1 mol % Au) distinguishes this precatalyst from previously reported precatalysts for alkyne hydrohydrazination with unsubstituted hydrazine, which are exclusively of the type (carbene)AuCl and operate under somewhat more forcing conditions (>80 °C and/or 5 mol % Au). In addition to establishing for the first time the beneficial role of appropriately configured phosphine ancillary ligands in Au-catalyzed alkyne hydrohydrazination chemistry, we view our results as expanding the catalyst "tool box" for chemists who seek to apply this methodology in chemical synthesis.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all reactions were set up inside a nitrogen-filled inert-atmosphere glovebox and worked up in air using benchtop procedures. When they were used within the glovebox, solvents were deoxygenated by sparging with nitrogen gas followed by passage through a double-column solvent purification system packed with alumina and copper-Q5 reactant (toluene and benzene), or alumina (dichloromethane) and storage over activated 4 Å molecular sieves. Ligands **L4**[17] and **L8**[18] and complexes **C3**[13] and **C6**[15] were prepared using literature methods; **L4** and **L8** are also available from commercial sources. All other materials including **L1**, **C2**, and **C7** were used as received from commercial sources. Column chromatography was carried out using neutral Silicycle Siliaflash 60 silica (particle size 40−63 μm; 230−400 mesh). NMR spectra were recorded at 300 K and referenced internally to the solvent employed. Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All coupling constants (J) are reported in hertz (Hz). In some cases fewer than expected independent ^{13}C NMR resonances were observed despite prolonged acquisition times. Mass spectra were obtained using ion trap (ESI) instruments operating in positive mode, and GC data were obtained on an instrument equipped with a SGE BP-5 column (30 m, 0.25 mm i.d.).

Synthesis of L5. A method directly analogous to that employed in the preparation of OTips-DalPhos (**L4**)[17] was used, whereby ClSi(O*t*Bu)$_3$ was used in place of ClSi(*i*Pr)$_3$. The crude product was purified by column chromatography using a 1/100 (EtOAc/hexanes)

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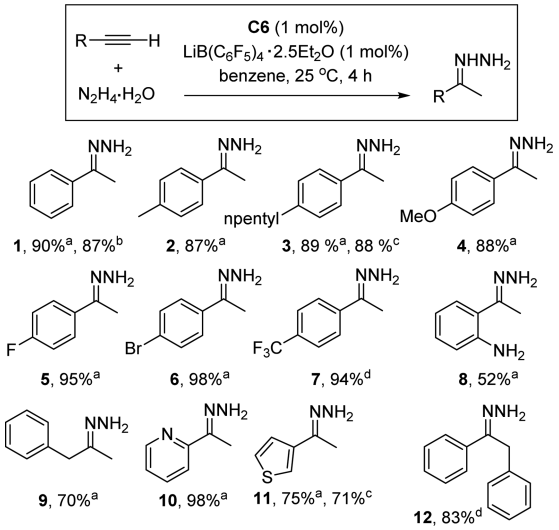
Scheme 4. Substrate Scope for the C6-Catalyzed Hydrohydrazination of Alkynes[a]



[a]Following GP3 or GP4 (see the Experimental Section) with estimated conversion to product stated on the basis of ^{1}H NMR data using trimethoxybenzene as an internal standard. [b]Reaction employing 1-phenyl-2-trimethylsilylacetylene in place of phenylacetylene. [c]Isolated yield of the derived diazine (**3′** or **11′**; see the Supporting Information). [d]Employing 5 mol % each of **C6** and $LiB(C_6F_5)_4{\cdot}2.5Et_2O$, 90 °C, 14 h, with isolated yield stated for **12**.

eluent system to afford the target product as a white powder (90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66−7.65 (m, 1H, ArH), 7.27−7.24 (m, 1H, ArH), 7.23−7.19 (m, 1H, ArH), 6.91−6.88 (m, 1H, ArH), 1.98−1.96 (m, 6H, AdH), 1.87−1.86 (m, 12H, AdH), 1.65 (s, 12H, AdH), 1.37 (s, 27H, *t*BuH). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 160.4 (d, J_{CP} = 22.6 Hz), 137.1, 129.4, 124.6 (d, J_{CP} = 27 Hz), 119.4, 119.2, 73.6, 42.0 (d, J_{CP} = 14 Hz), 37.3, 37.0, 36.8, 31.5, 29.0 (d, J_{CP} = 8.7 Hz). $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$): δ 11.7. HRMS: *m*/*z* ESI$^+$ found 641.4149 $[M + H]^+$, calculated for $C_{38}H_{62}O_4PSi$ 641.4155.

General Procedure for the Synthesis of Au Complexes (GP1). In air, a 100 mL round-bottom Schlenk flask was charged with a magnetic stir bar, phosphine ligand (0.41 mmol), and dichloromethane (30 mL). To this mixture was added a mixture of $AuCl(SMe_2)$ (0.41 mmol, 120.8 mg) in dichloromethane (50 mL). The reaction vessel was covered in Al foil to circumvent light-induced decomposition and was connected to a Schlenk apparatus. The headspace of the reaction flask was evacuated briefly and back-filled with nitrogen gas, and magnetic stirring was initiated. After 2 h, the reaction mixture was concentrated in vacuo. In air, the resulting residue was washed with acetone (2 × 10 mL) and was dried in vacuo to afford the target product.

General Procedure for the Synthesis of Au Complexes (GP2). Under a nitrogen atmosphere, a 50 mL round-bottom Schlenk flask was charged with a magnetic stir bar, $HAuCl_4{\cdot}H_2O$ (1.45 mmol, 0.492 g), and water (1.5 mL), and magnetic stirring was initiated. To this mixture was added dropwise 2,2′-thiodiethanol (4.4 mmol) over the course of 0.5 h, during which time the solution changed from an orange-yellow emulsion to clear and colorless. The Schlenk flask was then opened, and against a counterflow of nitrogen the phosphine ligand (1.45 mmol) was added in a single portion, followed by the addition of ethanol (4.5 mL). The Schlenk flask was then resealed under nitrogen, and magnetic stirring was continued for 3 h. The resulting mixture was then filtered in air and was washed with acetone (2 × 15 mL), diethyl ether (15 mL), and pentane (15 mL). The remaining solid was then dried in vacuo to afford the target product.

Compound ***C1***. The title complex was synthesized via GP2 from **L1** and was isolated as a white solid in 88% yield. A single crystal suitable for X-ray diffraction was obtained via vapor diffusion of pentane into a dichloromethane solution of **C1.** ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, J = 2.1 Hz, 1H, PyrH), 7.74−7.72 (m, 2H, ArH), 7.55−7.53 (m, 2H, ArH), 7.39−7.36 (m, 3H, ArH), 7.35−7.27 (m, 4H, ArH), 7.23−7.16 (m, 4H, Ar−H), 6.79 (d, J = 2.1 Hz, 1H, PyrH), 0.90 (d, J = 16.6 Hz, 9H, *t*Bu), 0.79 (d, J = 16.5 Hz, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 149.4, 141.5, 140.2, 140.1, 133.0−126.0 (overlapping signals), 120.0, 114.7, 37.3 (overlapping signals), 29.5 (overlapping signals). $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$): δ 48.2. Anal. Calcd for $C_{32}H_{35}AuClN_4P$: C, 52.01; H, 4.77; N, 7.58. Found: C, 51.87; H, 4.62; N 7.68.

Compound ***C4***. The title complex was synthesized via GP2 from **L4** and was isolated as a white solid in 91% yield. A single crystal suitable for X-ray diffraction was obtained via vapor diffusion of pentane into a dichloromethane solution of **C4**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73−7.68 (m, 1H, ArH), 7.38−7.28 (m, 1H, ArH), 7.03−6.96 (m, 2H, ArH), 2.23−2.19 (m, 12H, AdH), 2.02 (s, 6H, AdH), 1.85−1.80 (m, 3H, $CH(CH_3)_2$), 1.71 (s, 12H, AdH), 1.20−1.18 (m, 18H, $CH(CH_3)_2$). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 135.3, 132.1, 120.0, 118.8 (d, J_{CP} = 12.6 Hz), 112.9, 42.5−42.0 (overlapping signals), 36.3, 28.5 (d, J_{CP} = 16.4 Hz), 18.2, 13.6. $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$): δ 51.1. Anal. Calcd for $C_{35}H_{55}AuClOPSi$: C, 53.65; H, 7.08; N, 0. Found: C, 53.49; H, 7.17; N < 0.5.

Compound ***C5***. The title complex was synthesized via GP2 from **L5** and was isolated as a white solid in 90% yield. A single crystal suitable for X-ray diffraction was obtained via vapor diffusion of pentane into a dichloromethane solution of **C5**. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.56−8.51 (m, 1H, ArH), 7.56−7.54 (m, 1H, ArH), 7.43−7.40 (m, 1H, ArH), 7.06 (t, J = 7.5 Hz, 1H, ArH), 2.34−2.32 (br m, 6H, AdH), 2.21 (br s, 6H, AdH), 2.02 (br s, 6H, AdH), 1.75−1.69 (br m, 12H, AdH), 1.40 (s, 27H, O*t*Bu). $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ 156.1, 146.4 (d, J_{CP} = 23.9 Hz), 132.9, 121.2 (d, J_{CP} = 14.4 Hz), 120.6 (d, J_{CP} = 4.7 Hz), 116.0 (d, J_{CP} = 41.5 Hz), 74.9, 42.1 (d, J_{CP} = 23.9 Hz), 41.8, 36.5, 31.9, 28.9 (d, J_{CP} = 10.3 Hz). $^{31}P\{^1H\}$ NMR (202.4 MHz, $CDCl_3$): δ 97.4. Anal. Calcd for $C_{38}H_{61}AuClO_4PSi$: C, 52.26; H, 7.04; N, 0. Found: C, 52.31; H, 7.44; N, <0.5.

Compound ***C8***. The title complex was synthesized via GP1 from **L8** and was isolated as a white solid in 96% yield. A single crystal suitable for X-ray diffraction was obtained via vapor diffusion of diethyl ether into a dichloromethane solution of **C8**. The NMR spectra of **L8** and derived complexes are rendered complex due to a combination of second order phenomena and dynamic behavior involving the chiral phosphaadamantyl cage (CgP)/P(*o*-tolyl)$_2$ moiety.[18] ^{1}H NMR (CD_2Cl_2, 500 MHz): 8.62−8.58 (m, 1H, ArH), 7.65−7.62 (m, 1H, ArH), 7.55−7.52 (m, 1H, ArH), 7.37−7.31 (m, 4H, ArH), 7.28−7.25 (m, 1H, ArH), 7.16−7.11 (m, 2H, ArH), 6.75 (m, 2H, ArH), 2.90−2.88 (m, 1H, CgPH), 2.63 (br, 3H, CgPH), 2.33 (s, 3H, CgPH or $ArCH_3$), 2.12−1.84 (m, 4H, CgPH), 1.57 (s, 2H, CgPH), 1.45 (s, 4H, CgPH), 1.31 (s, 3H, CgPH or $ArCH_3$), 0.94−0.89 (m, 2H, CgPH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.4 MHz): 9.22 (d, J_{PP} = 207 Hz), 4.92 (d, J_{PP} = 207 Hz). Anal. Calcd for $C_{30}H_{34}AuClO_3P_2$: C, 48.87; H, 4.65; N, 0. Found: C, 48.61; H, 4.73; N < 0.5.

Compound ***C9***. The title complex was synthesized via GP1 from **L8** (using 2 equiv of $AuCl(SMe_2)$) and was isolated as a yellow solid in 97% yield. A single crystal suitable for X-ray diffraction was obtained via vapor diffusion of diethyl ether into a dichloromethane solution of **C9**. The NMR spectra of **L8** and derived complexes are rendered complex due to a combination of second order phenomena and dynamic behavior involving the chiral phosphaadamantyl cage (CgP)/P(*o*-tolyl)$_2$ moiety.[18] ^{1}H NMR (CD_2Cl_2, 500 MHz): 8.89−8.85 (m, 1H, ArH), 7.82−7.78 (m, 1H, ArH), 7.60−7.55 (m, 3H, ArH), 7.54−7.51 (m, 1H, ArH), 7.47−7.45 (m, 1H, ArH), 7.29−7.26 (m, 1H, ArH), 7.22−7.15 (m, 2H, ArH), 6.95−6.91 (m, 1H, ArH), 6.38−6.33 (m, 1H, ArH), 2.89−2.88 (m, 3H, CgPH), 2.80 (s, 3H, CgPH), 2.35−2.32 (m, 1H, CgPH), 2.05−1.90 (m, 5H, CgPH), 1.60−1.56 (m, 4H, CgPH and/or $ArCH_3$), 1.49−1.43 (m, 6H, CgPH and $ArCH_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202.4 MHz): 9.10 (d, J_{PP} = 51 Hz), 4.47 (d, J_{PP} = 51 Hz). Anal. Calcd for $C_{30}H_{34}Au_2Cl_2O_3P_2$: C, 37.15; H, 3.54; N, 0. Found: C, 37.33; H, 3.72; N, <0.5.

General Catalytic Procedure for the Formation of Imines from Terminal Alkynes (GP3). Unless specified otherwise in the

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text, **C6** (0.002 mmol) and $LiB(C_6F_5)_4{\cdot}2.5Et_2O$ (0.002 mmol) were placed as a stock solution in C_6D_6 (200 μL total delivered) in a screw-capped vial containing alkyne (0.2 mmol), hydrazine hydrate (0.24 mmol), C_6D_6 (400 μL), and a small magnetic stir bar. The vial was sealed with a cap containing a PTFE septum, removed from the glovebox, and placed in a temperature-controlled aluminum heating block set at 25 °C, and vigorous magnetic stirring was initiated for 4 h.

General Catalytic Procedure for the Formation of Imines from Internal Alkynes (GP4). Unless specified otherwise in the text, **C6** (0.02 mmol), $LiB(C_6F_5)_4{\cdot}2.5Et_2O$ (0.02 mmol), alkyne (0.4 mmol), hydrazine hydrate (0.48 mmol), and benzene (1.2 mL) were placed in a screw-capped vial containing a small magnetic stir bar. The vial was sealed with a cap containing a PTFE septum, removed from the glovebox, and placed in a temperature-controlled aluminum heating block set at 90 °C, and vigorous magnetic stirring was initiated for 16 h.

Workup Method A (Purification via Chromatography). Upon completion following **GP3** or **GP4**, the reaction vial was cooled to room temperature (if needed). The reaction mixture was filtered through a Celite/silica plug and washed with dichloromethane (3 × 20 mL). From the collected eluent, the solvent was removed in vacuo via rotary evaporation and the compound was purified by flash column chromatography on silica gel.

Workup Method B (Procedure for the Preparation of Samples for NMR Quantification). Upon completion following GP3 or GP4, the reaction vial was removed from the heating block and cooled to 4 °C, whereby an internal standard of trimethoxybenzene (0.04 mmol) was added to the reaction mixture. The reaction mixture was then filtered through Celite, and the eluent was collected and subjected to NMR analysis, with yields of product reported relative to the internal standard on the basis of integrated ^{1}H NMR signals.

Crystallographic Solution and Refinement Details. Crystallographic data were obtained between 193 and 213 K on a Bruker D8/APEX II CCD diffractometer equipped with a CCD area detector using graphite-monochromated Mo Kα (α = 0.71073 Å) or Cu Kα (α = 1.54178 Å) radiation employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Data reduction, Lorentz−polarization correction, and absorption correction (Gaussian integration; face-indexed) were each performed. Structure solution by using direct methods, Patterson methods, or intrinsic phasing was carried out, followed by least-squares refinement on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters, while all hydrogen atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom. Additional information is contained in the deposited CIFs (CCDC 1550225−1550228, 1550230−1550231).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00373.

Complete characterization data for catalytic reaction products, including NMR spectra, and selected tabulated crystallographic data (PDF)

Accession Codes

CCDC 1550225−1550228 and 1550230−1550231 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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