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Syn-Insertion of Alkynes into Gold−Phosphito Bonds: Stereoselectivity and Reversible Protodeauration

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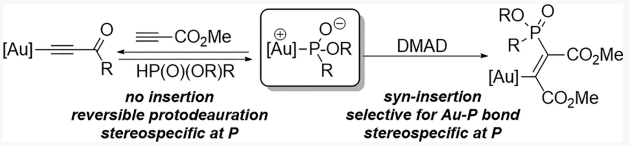
ABSTRACT: The susceptibility of gold phosphito compounds to undergo alkyne insertion into gold−phosphorus bonds has been investigated. An electron-deficient alkyne (DMAD) underwent *syn*-insertion into the gold−phosphorus bond to generate a *Z*-vinylgold species, whereas electron-rich internal alkynes were unreactive. When a P-chiral phosphinate was used as a probe, the protodeauration and insertion steps were found to be stereospecific. In contrast to the insertion chemistry observed with DMAD, electron-deficient terminal alkynes generated alkynylgold compounds and released secondary phosphites through a reversible protodeauration process.



INTRODUCTION

The insertion of alkynes into metal-element bonds remains one of the most valuable reactions in organometallic chemistry. The intense interest in this area stems from the vast number of applications this fundamental reaction has in small molecule[1−6] and polymer chemistry.[7−10] Furthermore, alkyne insertion chemistry provides an atom-efficient approach to the synthesis of vinylmetal species.[11−16] Historically, gold compounds were thought to be unreactive toward this process. However, Teles' pioneering work demonstrated that cationic gold compounds activated alkynes toward nucleophilic attack through coordination of the π-system.[17] This outer-sphere pathway generated a vinylgold species and resulted in an overall *anti*-addition to the alkyne. Following this work, a vast array of alkyne functionalization reactions have been reported.[18−27]

In contrast, an inner-sphere alkyne insertion reaction generates a formal *syn*-insertion product.[28] The mechanism of this process also entails initial coordination of the alkyne to the gold; however, the next step is a migratory insertion of the alkyne into the gold−element bond to generate the vinylgold species. Despite the intense interest in this area, *syn*-insertions are rare.[28] Moreover, formal alkyne *syn*-insertions into well-defined gold-heteroatom bonds are exceedingly rare.

With the hope of developing gold-catalyzed processes for the preparation of functionalized alkenes, several research teams investigated this process and found electron-rich internal alkynes such as diphenyl acetylene and 4-octyne to be generally unreactive toward *syn*-insertions, whereas electron-deficient alkynes displayed a range of reactivity. Toste and Bergman reported no reaction between amidogold compounds and electron-rich internal alkynes, but an electron-poor alkene, acrylonitrile, successfully inserted into the gold−nitrogen bond.[29] Nolan found that gold phenoxide compounds of the type (NHC)Au-OAr were resistant toward the insertion of diphenylacetylene.[30] There are also examples of intramolecular *anti*-insertions into gold−heteroatom bonds. Bertrand and Hashmi reported *anti*-aminoauration[31] and *anti*-phosphinoauration of alkynylaniline derivatives.[32]

It should be noted that treating a fluorogold species with 3-hexyne resulted in the reversible insertion of the alkyne into the Au−F bond.[33] An (*E*)-vinylgold compound was observed. The proposed mechanism entailed the initial loss of the fluoride, coordination of the hexyne to the gold center, and *anti*-addition of the fluoride to the coordinated alkyne.

Reactions between electron-deficient alkynes and LAuX species are complex and generate a range of vinylgold compounds (Scheme 1). The regiochemistry and stereochemistry of these reactions depend upon the identity of the heteroatom and the supporting ligands. Several studies found that phosphine ligands were not entirely innocent and generated zwitterionic vinylgold compounds resulting from insertion of the alkyne into the gold−ligand bond. Kuniyasu and Kambe reported reactions between gold thiolate complexes of the type (Ph_3P)AuSAr and dimethyl acetylenedicarboxylate (DMAD).[34] Vinylgold compounds were generated from the insertion of the alkyne into the Au−PR_3 bond. The Au−S bond was *retained* in these reactions. Bourissou investigated terminal and internal alkynes' reactivity with silylgold compounds and discovered that DMAD underwent a *syn*-insertion into the gold−silicon bond.[35]

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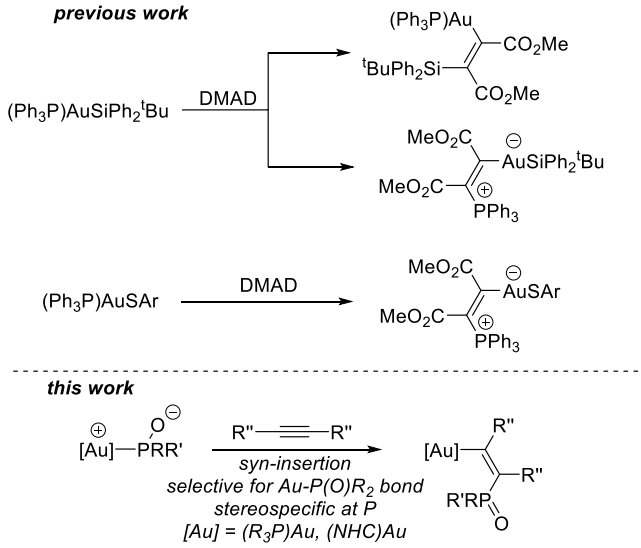
Scheme 1. *Syn*-Insertions into Gold−Heteroatom Bonds[34,35]

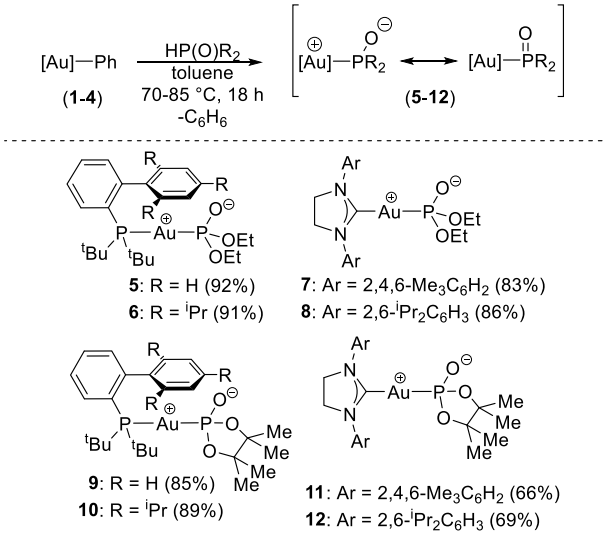


To gain insight into the susceptibility of gold phosphito compounds to undergo alkyne insertion reactions, we have investigated the reactivity of discrete species with a range of internal and terminal alkynes and defined the key reaction parameters for the design of a successful *syn*-insertion reaction.

RESULTS AND DISCUSSION

Synthesis of Model Compounds. Several gold phosphito complexes (**5**−**12**) were generated through protodeauration reactions between arylgold precursors (**1**−**4**) and secondary phosphites (Scheme 2).[36−40] The bulky Buchwald and carbene

Scheme 2. Synthesis of Model Compounds



ligands were selected to minimize reversible ligand redistribution reactions commonly observed with gold phosphito compounds.[37,39] Both cyclic and acyclic phosphites afforded high yields of the target gold compounds. Compounds **5**−**12** were isolated as powders and exhibited a resonance for the $P(O)(OR)_2^-$ fragment in the ^{31}P NMR spectrum between δ 111 and 121 ppm with $^2J_{PP}$ between 473 and 491 Hz for **5**, **6**, **9**, and **10**. While two bonding modes are known for metal phosphito compounds, spectroscopic[41−43] and computational[44] evidence suggests the bonding mode of $[PO_3R_2]^-$ groups in **5**−**12** is consistent with a κ^1-P(III) O-anionic phosphito donor.[45,46]

The structures of compounds **5** and **7** were determined by single-crystal X-ray diffraction (Figures 1 and 2). The gold−

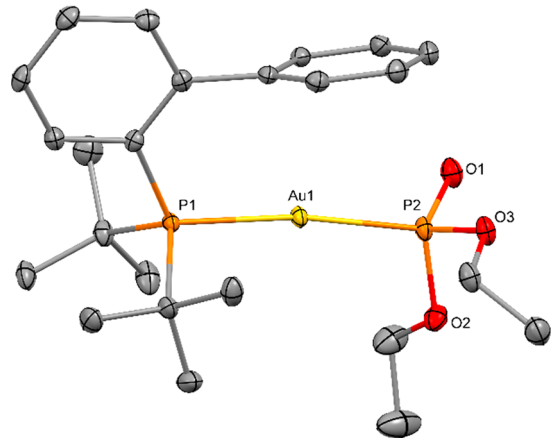


Figure 1. Structure of **5**. Thermal ellipsoids are displayed at 50% probability, and hydrogens are omitted for clarity. Selected bond distances (Å) and angles (deg): Au(1)−P(2) = 2.3065(5), Au(1)−P(1) = 2.3470(4), P(2)−O(1) = 1.4833(14), P(2)−O(3) = 1.6131(13), P(2)−Au(1)−P(1) = 172.291(16), O(1)−P(2)−Au(1) = 118.95(6), O(2)−P(2)−Au(1) = 108.29(5).

phosphorus bond distances are different in **5**, with the Au−PR_3 distance found to be the longer of the two (2.3065(5) vs 2.3470(4) Å). The P−Au−P angle deviates from linearity (172.291(16)°), and the Au^+−P−O^- angle (118.95(6)°) is larger than the two Au^+−P−OEt angles (110.53(5)° and 108.29(5)°). The gold−carbon bond distances of the two independent molecules of **7** are indistinguishable (2.054(4) and 2.056(4) Å), whereas the C−Au−P angles are different (177.76(12)° and 174.51(11)°) but do not deviate from linearity as much as the P−Au−P angle found in **5**. The Au−P bond lengths found in **7** (2.2903(10) and 2.2929(10) Å) are nearly identical to the corresponding bond lengths in **5**, suggesting that the *trans*-influence of the carbene and phosphine ligands is comparable. Similar to **5**, the Au^+−P−O^- angles (122.5(1)°, 121.7(1)°) are significantly larger than the two Au^+−P−OEt angles (103.1(1)−110.5(1)°).

Compounds **5**−**12** are hygroscopic, and although crystals of **5** grew in an anhydrous state, three molecules of adventitious water were found in the unit cell of **7**. Two of these water molecules link two molecules of **7** together through a hydrogen-bonded chain, while the third hydrogen bonds to only a single molecule of **7**. No aurophilic interactions were found in the packing of **5** or **7**.

Reactivity of Model Compounds. The reactivity of the model compounds toward alkyne insertion was investigated using a range of alkynes (Table 1). When electron-rich alkynes such as diphenylacetylene or 5-decyne were used, no insertion products were observed with **5**−**12**. Prolonged stirring (1 wk, 80 °C) or increasing the temperature (110 °C) led to decomposition and the formation of intractable mixtures. Increasing the amount of the alkyne to 100 equiv was also unsuccessful at 80 or 110 °C.

Several functionalized alkynes were screened for activity toward the insertion reaction (Table 1). Heating suspensions

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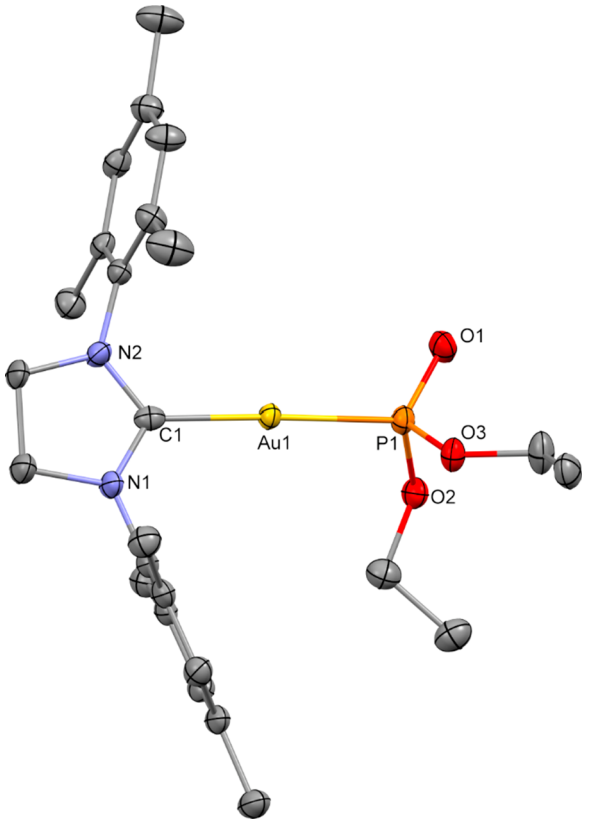
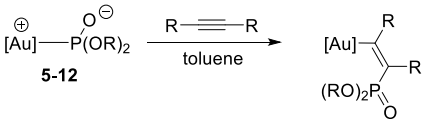


Figure 2. Structure of **7**. Thermal ellipsoids are displayed at 50% probability, and the hydrogens as well as water molecules are omitted for clarity. Selected bond distances (Å) and angles (deg): Au(1)−C(1) = 2.056(4), Au(1)−P(1) = 2.2903(10), P(1)−O(1) = 1.481(3), P(1)−O(3) = 1.621(3), C(1)−Au(1)−P(1) = 177.76(12), O(1)−P(1)−Au(1) = 121.74(14), N(1)−C(1)−Au(1) = 124.7(3), N(2)−C(1)−N(1) = 109.7(4).

Table 1. Alkyne Insertion into Gold−Phosphorus Bonds[a]



Cmpd.	R—≡—R	equiv	Temp(°C)	Time(d)	Cnv.[b]
5-12	R = Bu, Ph C(O)NEt$_2$ P(O)Ph$_2$[c]	10, 100	80, 110	7	-
5	DMAD	4[d]	80	2	84
7	DMAD	4[e]	80	2	76

[a]Reaction conditions: **5−12** (0.13−0.16 mmol) in toluene (1.0 mL) unless specified. [b]Based upon isolated material. [c]The reaction was heterogeneous due to the low solubility of dppaOO in toluene. [d]1.6 mmol of **5** was used along with 5.0 mL of toluene. [e]1.6 mmol of **7** was used along with 5.0 mL of toluene.

of bis(diphenylphosphino)acetylene dioxide (dppaOO)[47] with **5−12** resulted in recovered starting materials after stirring for a week at 80 °C, whereas heating to 110° resulted in decomposition. Similarly, tetraethyl-acetylenedicarboxamide[48] was unreactive toward the insertion reaction at lower temperatures, and heating **5−12** with an excess of the dicarboxamide to 110 °C resulted in the formation of intractable mixtures.

Analogous reactions using an electron-deficient alkyne (DMAD) afforded a range of products depending on the ancillary ligand attached to the gold as well as the phosphite. Substrates bearing bulky phosphine or carbene ligands (**6**, **8**, **10**, **12**) were unreactive, and starting materials were recovered after heating (80 °C, 48 h). When the temperature was increased (110 °C), decomposition and the formation of intractable mixtures were observed. The substrates containing cyclic phosphites also generated mixtures, and vinylgold compounds could not be isolated.

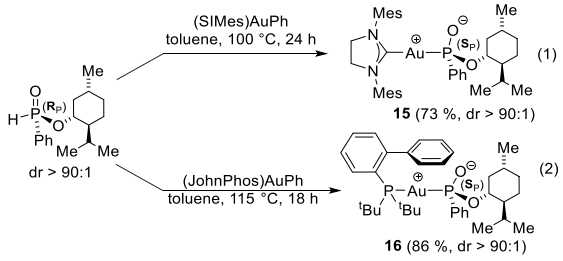
In contrast, substrates bearing smaller supporting ligands and an acyclic phosphite (**5**, **7**) afforded vinylgold compounds (**13**, **14**, Table 1). Monitoring the reaction of **7** with DMAD by ^{31}P NMR spectroscopy revealed the clean conversion of the gold phosphito compound (**7**, δ 112.3 ppm) into the vinylgold species (**14**, δ 18.3 ppm). The transformation of the metal phosphite into a phosphonate was easy to follow since there was a 94 ppm change in the chemical shift of the $-P(O)(OEt)_2$ fragment. In contrast with several previous reports describing the reactivity of $(R_3P)AuX$ compounds with activated alkynes, DMAD exclusively inserted into the Au−phosphito bond.[34,35] No insertion of DMAD into the Au−carbene bond was observed.

Monitoring the formation of **13** from **5** yielded similar observations. Clean insertion into the gold−phosphito bond was observed, and no intermediates or insertion into the gold−phosphine bond were found. Of note was the observation of a $^4J_{PP}$ of 14.6 Hz in the JohnPhos ligated vinylgold species (**13**).

Two electron-withdrawing groups were required for a successful insertion reaction. Treating **5−12** with methyl phenylpropiolate (Ph-C≡CCO$_2$Me, 4−100 equiv) resulted in recovered starting materials (80 °C, 48 h). Prolonged stirring or increasing the temperature to 110 °C resulted in decomposition. These observations are in contrast with the *syn*-insertion into Au−Si bonds that Bourissou observed when $(Ph_3P)AuSiPh_3$ was treated with methyl phenylpropiolate.[49]

The structures of **13** and **14** were determined by single-crystal X-ray crystallography and revealed the *syn*-insertion of DMAD into the gold phosphorus bonds of **5** and **7** (Figure 3, Table 2), resulting in a *Z*-configuration. The alkene geometry deviates from planarity in **13** and **14**, as evidenced by the torsion angles (Table 2). There were no aurophilic interactions in the structures of **13** or **14**.

The stereochemistry of the protodeauration and insertion reactions was investigated using a P-chiral phosphinate, ($\boldsymbol{R}_P$)(−)menthyl phenylphosphinate.[50−55] Treatment of (SIMes)AuPh or (JohnPhos)AuPh with the phosphinate generated high yields of the metal phosphinito species through a protodeauration reaction (eqs 1 and 2).[36] The reaction was



stereospecific, as evidenced by NMR spectroscopic data. It is worth noting that **15** and **16** are configurationally stable, and no epimerization was observed upon heating to 110 °C.

X-ray quality crystals of **15** were obtained by simply cooling the crude reaction mixture (Figure 4). Analysis of this structure

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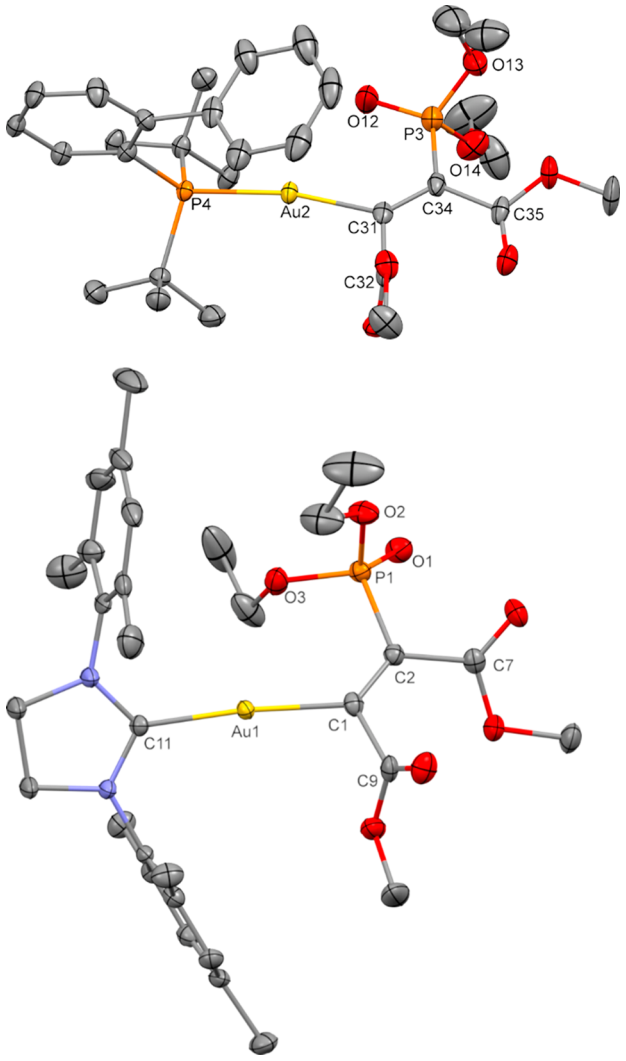
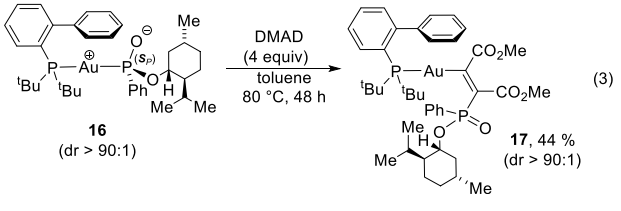


Figure 3. Structures of alkyne insertion products (**13**, **14**). Thermal ellipsoids are displayed at 50% probability, and the hydrogens are omitted for clarity.

revealed that the protodeauration occurred with *retention* of the configuration. This structure also sheds light on our recent report regarding the stereospecific protodeauration and transmetalation reactions between gold and palladium.[36]

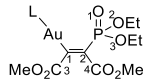
Similar to the reactions of **5** and **7** with DMAD, treatment of **16** with DMAD afforded a vinylgold compound (**17**, eq 3). It



(3)

should be noted that the reactivity of **16** toward insertion was sluggish compared to **5** or **7**, and only moderate conversion was observed. After heating for 48 h at 80 °C, 45% of **16** remained unreacted. Monitoring the reaction by ^{1}H and ^{31}P NMR spectroscopy revealed the emergence of a single set of signals for **17** (^{31}P δ: 63.6, 29.0; $^{4}J_{PP}$ = 12.3), confirming that the reaction was stereospecific at phosphorus.

Table 2. Selected Bond Distances (Å) and Angles (deg) for the *Syn*-Insertion Products (13, 14)



	13	14
distances		
Au–L	2.2986(11)	2.020(2)
Au–C=	2.060(4)	2.041(3)
C=C	1.353(6)	1.347(4)
=C–P	1.807(4)	1.808(3)
P=O_1	1.470(3)	1.465(2)
angles		
L–Au–C_1	168.74(13)	174.46(10)
Au–C_1=C_2	127.6(3)	131.8(2)
C_1=C_2–P	120.9(3)	124.6(2)
C_2–P–O_1	113.37(19)	112.17(12)
torsion angles		
Au–C_1=C_2–P	8.4(6)	2.7(4)
Au–C_1=C_2–C_4	168.3(3)	179.86(19)
C_3–C_1=C_2–C_4	5.9(6)	0.8(4)
C_3–C_1=C_2–P	177.3(3)	176.31(19)

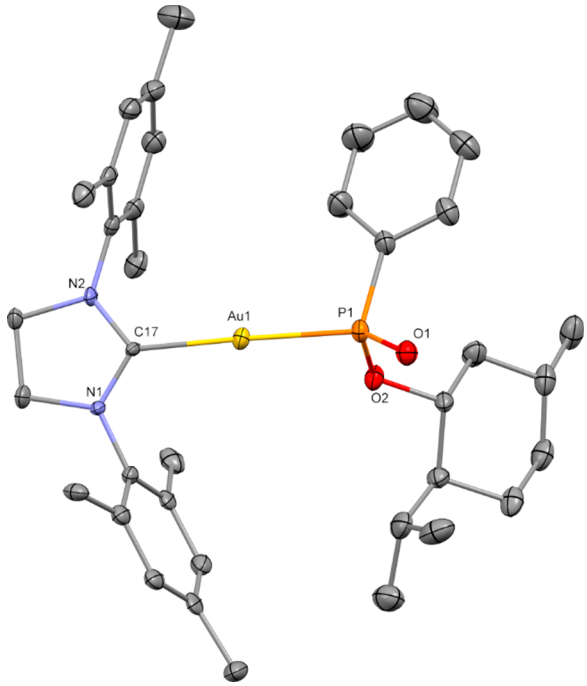


Figure 4. Structure of **15**. Hydrogen atoms are omitted, and thermal ellipsoids are displayed at 50% probability. Selected bond distances (Å) and angles (deg): Au(1)–P(1) = 2.297(3), Au(1)–C(17) = 2.090(10), P(1)–O(1) = 1.508(7), P(1)–O(2) = 1.620(7), C(17)–Au(1)–P(1) = 175.7(3), O(1)–P(1)–Au(1) = 121.0(3), O(1)–P(1)–O(2) = 111.0(4), O(1)–P(1)–C(1) = 109.0(5).

Protodeauration between the vinylgold species and a secondary phosphite would be the step in a catalytic cycle that forms the vinyl phosphonate and regenerates the gold phosphito species. Treatment of **13** with $HP(O)(OEt)_2$ does indeed generate **5** and the vinyl phosphonate (90 °C, 20 h). However, the development of a catalytic process was hindered by the observation that an uncatalyzed double-addition reaction occurs between DMAD and $HP(O)(OEt)_2$ (2 equiv) under the insertion conditions (80 °C, 2 days).[56] A

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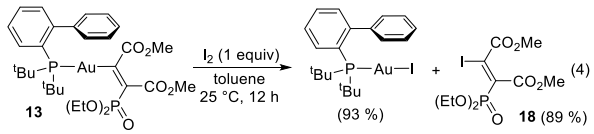
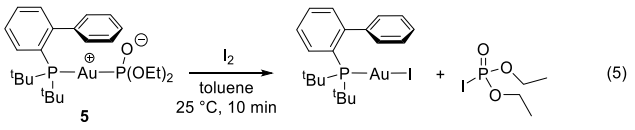
successful catalytic approach needs to circumvent this background reaction.

To this end, we investigated the possibility of replacing the protodeauration step with iodination in order to eliminate the need for the secondary phosphite. This alternative approach would convert the vinylgold intermediate into an iodovinyl phosphonate and an iodogold species. The latter could be transformed into a gold phosphito species through transmetalation with $M[P(O)R_2]$.[57] Treatment of **13** with I_2 afforded (JohnPhos)AuI and a (*Z*)-*β*-iodo-vinylphosphonate (**18**) under mild conditions (eq 4).[58]



Although the reaction using discrete species was successful, the development of a catalytic process was prevented by the observation that iodine reacts rapidly with **5** to generate (JohnPhos)AuI and $IP(O)(OEt)_2$ (eq 5).[59] As a result, any gold phosphito intermediates would be rapidly consumed by iodine prior to alkyne insertion.



We were able to increase the scale of the iodination reaction. Treatment of a 1.00 g sample of **13** (1.29 mmol) with iodine afforded **18** in 89% yield. Although a process that is stoichiometric in gold is generally not desirable, it should be noted that the gold is not sacrificial in this reaction. The gold was recovered as (JohnPhos)AuI (93%) and used in subsequent reactions.

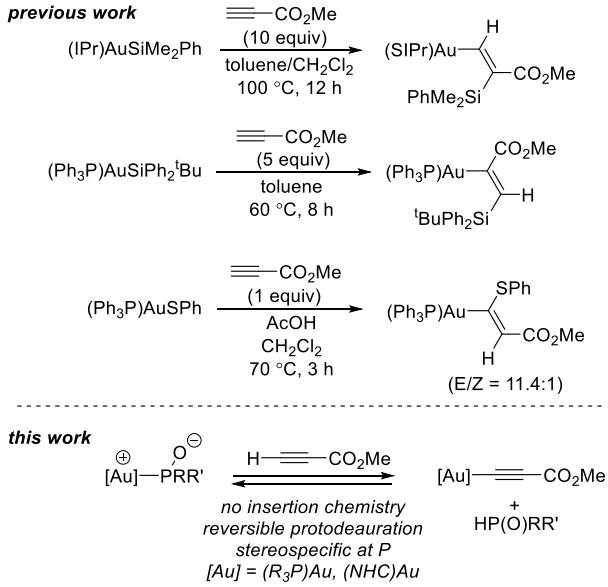
Reactivity of Terminal Alkynes. The reactivity of terminal alkynes was also investigated. Previous reports found that the regioselectivity of the insertion reaction was sensitive to the supporting ligand attached to the gold. Bourissou found that methyl propiolate regioselectively inserted into the gold−silicon bond of $(Ph_3P)AuSiMe_2Ph$ to generate a vinylgold species with a *β*-carboxylate fragment.[35,49] Subsequent work revealed that changing the supporting ligand to an N-heterocyclic carbene reversed the regioselectivity of the insertion reaction (Scheme 3).[60] Ananikov reported the acetic acid promoted insertion of methyl propiolate into the gold−phosphorus bond of gold thiolate compounds (Scheme 3).[61]

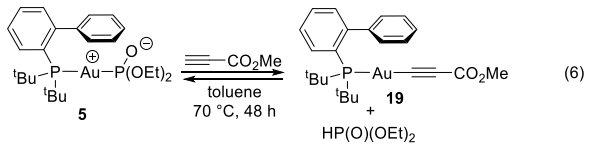
To probe the reactivity of terminal alkynes toward the insertion reaction, a model gold phosphito compound (**5**) was treated with terminal alkynes. Adding 1-hexyne to **5** (80 °C for 48 h) resulted in the recovery of starting materials. No insertion products were observed. Switching to an electron-deficient alkyne (methyl propiolate) did not generate insertion products; however, analysis of the reaction mixture revealed the presence of an alkynylgold species ((JohnPhos)AuC≡CCO_2Me) and diethylphosphite. Instead of alkyne insertion, protodeauration occurred to generate the alkynylgold species along with a secondary phosphite (eq 6).

The protodeauration reaction was found to be reversible and influenced by the nature of the terminal alkyne. For electron-rich alkynes, the reaction highly favored the metal phosphite.[40] In contrast, significant amounts of the alkynylgold species were observed when electron-deficient alkynes were used. Although the focus of this work was insertion chemistry, this chemistry is noteworthy since examples of reversible protodeauration at gold(I) are rare.[62]

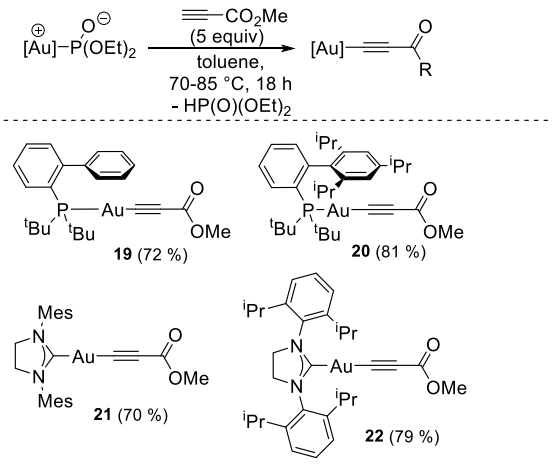
Building on these observations, a preparative method was devised for converting metal phosphito species into alkynylgold compounds. The scope of this process was investigated using the remainder of the gold phosphito compounds (Scheme 4). When methyl propiolate was used as a representative electron-deficient alkyne, compounds **5**−**8** were successfully converted into alkynylgold species (**19**−**22**)

Scheme 3. Regioselective Insertion of Terminal Alkynes into Gold−Silicon Bonds





Scheme 4. Synthesis of Alkynylgold Species from Gold Phosphites



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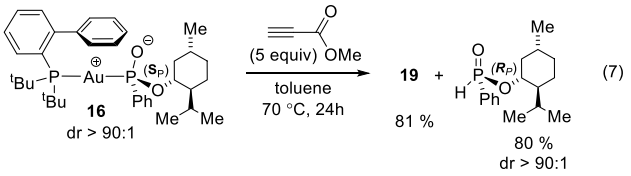
in moderate to good isolated yields. Even gold phosphito compounds containing bulky carbene or dialkylbiaryl ligands were successfully transformed using 5 equiv of the alkyne. Since the alkynylation reaction proceeded under base-free conditions, this process could be a practical approach to the synthesis of alkynylgold compounds bearing base-sensitive groups.[63,64]

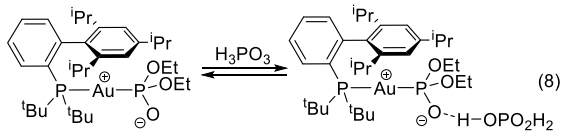
The stereochemical outcome of this reversible protodeauration reaction was investigated using a P-chiral gold phosphite (**16**). Treatment of **16** with methyl propiolate (eq 7) afforded



19, as well as (R_P)(−)menthyl phenylphosphinate. Thus, the protodeauration was found to be stereospecific and proceed with *retention* of the configuration. No epimerization of the phosphorus stereocenter was observed. It should be noted that the reaction of the phenylgold precursor (**1**) with secondary phosphites and (R_P)(−)menthyl phenylphosphinate was not reversible.

Inspired by Ananikov's report on the synthesis of *gem*-vinylgold thiolate complexes through the treatment of gold thiolates with methyl propiolate in the presence of carboxylic acids,[61] the effect of benzoic acid on the protodeauration reaction was investigated. No protodeauration was observed between **5** and benzoic acid (80 °C, 6 days). Adding methyl propiolate to this reaction (1:1−1:5 equiv) led to mixtures of **5** and **19** after heating (80 °C, 24 h). Using an excess of benzoic acid (1:10) significantly suppressed the alkynylation reaction, and unreacted **5** was the major species found in the crude reaction mixture. No vinylgold compounds were found in these reactions. Because of the observation that benzoic acid hydrogen bonds to **5**, it is reasonable to predict that an excess of benzoic acid will sequester the [Au$^+$]P-O$^-$ group and prevent the alkynylation reaction.

Since benzoic acid was unable to promote the insertion reaction, a stronger acid, H_3PO_3, was screened. The addition of H_3PO_3 (1 equiv) to solutions of **5**−**12** along with methyl propiolate (50 °C, 24 h) did not promote the insertion reaction. Monitoring the reactions using ^{31}P NMR spectroscopy revealed broadening of the resonance for the −P(O)-(OR)$_2$ fragment due to hydrogen bonding between the metal phosphite and H_3PO_3 (eq 8), but no insertion or protodeauration products were observed in the ^{1}H or ^{31}P NMR spectra.



To evaluate the ability of H_3PO_3 to cleave the gold−phosphorus bond, separate experiments were carried out between **5**−**12** and H_3PO_3. While the coordination of the acid to the metal phosphite was evident in the ^{31}P NMR spectrum, no cleavage of the gold−phosphorus bond was observed from these control reactions.

Cooling the reaction mixture containing **10** and H_3PO_3 afforded X-ray quality crystals of a H_3PO_3 adduct. The phosphorous acid interacts with **10** by forming hydrogen bonds with the phosphito oxygen (Figure 5). The oxygen−

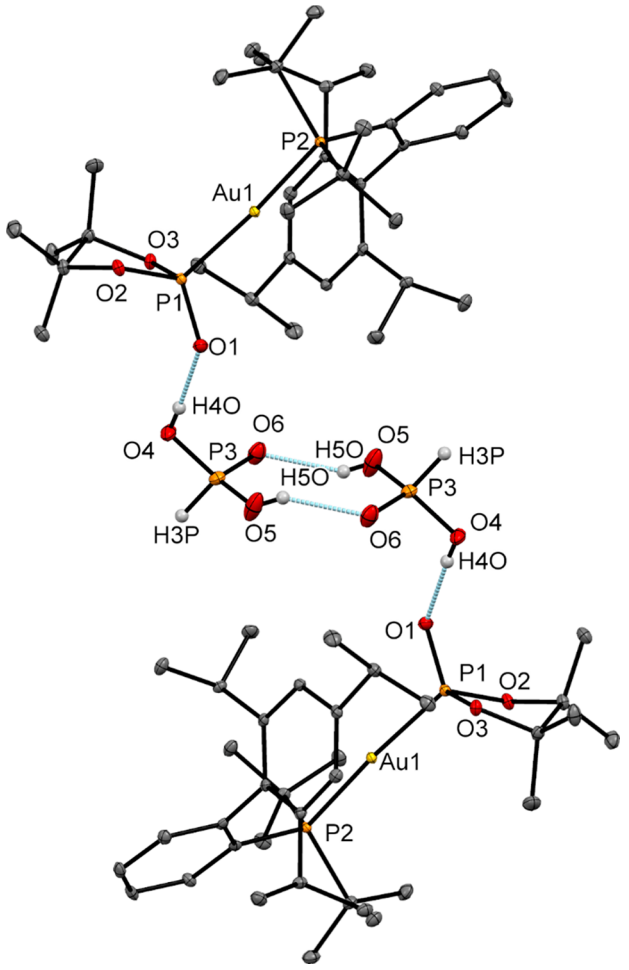


Figure 5. Structure of dimerized **10**·H_3PO_3. Thermal ellipsoids are displayed at 50% probability, and the hydrogens are omitted for clarity. Selected bond distances (Å) and angles (deg). Au(1)−P(1) = 2.2878(7), Au(1)−P(2) = 2.3261(7), P(1)−O(1) = 1.504(2), P(1)−Au(1)−P(2) = 171.53(2), O(1)−P(1)−O(2) = 112.82(12), O(1)−P(1)−Au(1) = 115.28(9). Hydrogen bonding: O(4)−O(1) = 2.476(3), O(5)−O(6) = 2.527(4), P(1)−O(1)−O(4) = 131.7(3), P(3)−O(6)−O(5) = 129.2(2).

oxygen bond distance is 2.476(3) Å, and the PO···H−O angle is 171(7)°. Two molecules of H_3PO_3 are connected through hydrogen bonds as well, which results in the linkage of two molecules of **10** through the dimerized H_3PO_3. Analysis of the extended structure reveals that the H_3PO_3 resides in channels surrounded by molecules of **10**. The two Au−P bond lengths are 2.2878(7) and 2.3261(7) Å, with the phosphine−gold bond being the longer of the two. The P−O$^-$ distance is longer (1.504(2) Å) than similar complexes which could be due to hydrogen bonding of the phosphorus acid.

In conclusion, electron-deficient internal alkynes insert into the Au−P bonds of gold phosphito compounds to generate (*Z*)-vinylgold species. When a P-chiral phosphinate was used as a model system, the protodeauration and alkyne insertion reactions were found to be stereospecific. In contrast to these findings, terminal alkynes did not show any propensity toward

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insertion. Instead, terminal alkynes participated in a reversible protodeauration reaction with the gold phosphito species to generate alkynylgold compounds and free phosphite.

EXPERIMENTAL SECTION

General Considerations. All reactions were carried out under a nitrogen atmosphere unless specified. Solvents were dried using CaH_2 or a Grubbs-type solvent purification system and distilled prior to use. The chlorogold precursors (JohnPhos)AuCl,[65] (^{t}BuXPhos)AuCl,[66] (SIMes)AuCl,[67] and (SIPr)AuCl[67] as well as tetraethyl-acetylenedicarboxamide[48] and bis(diphenylphosphino)acetylene dioxide[47] were prepared following literature procedures. The arylgold precursors were prepared following variations of literature procedures as described below.[68−72] The remaining reagents were obtained from commercial sources and used as received. $CDCl_3$ was dried over CaH_2 and distilled immediately prior to use while C_6D_6 was dried over activated molecular sieves (3 Å) and filtered through a 5 μm filter prior to use. ^{1}H NMR chemical shifts were determined by reference to residual nondeuterated solvent resonances, and $^{13}C\{^1H\}$ chemical shifts were determined by reference to deuterated solvent resonances. Coupling constants are given in hertz. $^{31}P\{^1H\}$ NMR spectra were referenced to external H_3PO_4 (0 ppm). ^{1}H and ^{13}C NMR resonances were assigned through analysis of 1D and 2D experiments. Elemental analyses were determined by Midwest Microlabs.

Preparation of Arylgold Precursors. General Method A. A vial (30 mL) was charged with LAuCl, $PhB(OH)_2$ (2 equiv), Cs_2CO_3 (2 equiv), and a magnetic stirring bar (in air). The vial was capped, and the atmosphere was exchanged for nitrogen using a vacuum manifold. After injecting isopropanol by syringe, the vial was placed in an aluminum block heater at 55 °C and stirred for 24 h. The arylgold compounds were separated from the solid residue by column chromatography. Chromatography details: flash (N_2 pressure), 35−40 g of SiO_2 (NEt_3 treated) per gram of crude arylgold compound, hexane:EtOAc (gradient 100:0−75:25). After removal of the volatiles, the residue was dissolved in CH_2Cl_2 and dried over $MgSO_4$. Filtration, concentration, and drying overnight afforded the (**1**−**4**) as white solids. If desired, **1**−**4** can be recrystallized by cooling saturated EtOAc solutions to −30 °C.

*Preparation of (JohnPhos)AuPh (**1**).* The title compound was prepared following general method **A** using (JohnPhos)AuCl (2.00 g, 3.77 mmol), $PhB(OH)_2$ (0.919 g, 7.54 mmol), Cs_2CO_3 (2.46 g, 7.55 mmol), and isopropanol (20 mL). After purification by column chromatography (R_f = 0.52, hexane:EtOAc 70:30), the title compound was isolated as a white solid (1.56 g, 72%).[72]

*Preparation of (^{t}BuXPhos)AuPh (**2**).* The title compound was prepared following general method **A** using (^{t}BuXPhos)AuCl (2.00 g, 3.04 mmol), $PhB(OH)_2$ (0.742 g, 6.09 mmol), Cs_2CO_3 (1.98 g, 6.08 mmol), and isopropanol (20 mL). After purification by column chromatography (R_f = 0.70, hexane:EtOAc 70:30), the title compound was isolated as a white solid (1.61 g, 76%).[72]

*Preparation of (SIMes)AuPh (**3**).* The title compound was prepared following general method **A** using (SIMes)AuCl (2.00 g, 3.71 mmol), $PhB(OH)_2$ (0.905 g, 7.42 mmol), Cs_2CO_3 (2.42 g, 7.43 mmol), and isopropanol (20 mL). After purification by column chromatography (R_f = 0.26, hexane:EtOAc 70:30), the title compound was isolated as a white solid (1.41 g, 65.4%). Anal. Calcd for $C_{27}H_{31}AuN_2$: C, 55.86; H, 5.38. Found: C, 55.97; H, 5.44. ^{1}H ($CDCl_3$, 25 °C): δ 7.02 (m, 4H, ArH), 6.97 (s, 4H, ArH), 6.84 (t, 1H, J = 7.0, ArH), 3.94 (s, 4H, $-CH_2N-$), 2.39 (s, 12H, −Me), 2.32 (s, 6H, −Me). $^{13}C\{^1H\}$ ($CDCl_3$, 25 °C): δ 216.2 (s, carbene C), 169.6 (s, quat), 140.6 (s, ArCH), 138.3 (s, quat), 135.9 (s, quat), 135.5 (s, quat), 129.6 (s, ArCH), 126.8 (s, ArCH), 124.7 (s, ArCH), 51.0 (s, $-CH_2N-$), 21.2 (s, −Me), 18.3 (s, −Me).

*Preparation of (SIPr)AuPh (**4**).* The title compound was prepared following general method **A** using (SIPr)AuCl (2.00 g, 3.21 mmol), $PhB(OH)_2$ (0.783 g, 6.42 mmol), Cs_2CO_3 (2.09 g, 6.41 mmol), and isopropanol (20 mL). After purification by column chromatography (R_f = 0.74, hexane:EtOAc 70:30), the title compound was isolated as a white solid (1.45 g, 68.4%). Anal. Calcd for $C_{33}H_{43}AuN_2$: C, 59.63; H, 6.52. Found: C, 59.85; H, 6.61. ^{1}H ($CDCl_3$, 25 °C): δ 7.39 (t, 2H, J = 7.7, ArH), 7.23 (d, 4H, J = 7.7, ArH), 6.99 (m, 4H, Ar-H), 6.82 (t, 1H, J = 7.0, ArH), 4.01 (s, 4H, $-CH_2N-$), 3.17 (sept, 4H, J = 6.8, −CH−), 1.50 (d, 12H, J = 6.8, −Me), 1.37 (d, 12H, J = 6.9, −Me). $^{13}C\{^1H\}$ ($CDCl_3$, 25 °C): δ 216.7 (s, carbene C), 170.2 (s, quat), 146.9 (s, quat), 140.6 (s, ArCH), 134.9 (s, quat), 129.5 (s, ArCH), 126.7 (s, ArCH), 124.4 (s, ArCH), 124.3 (s, ArCH), 53.9 (s, $-CH_2N-$), 29.1 (s, −CH−), 25.2 (s, −Me), 24.2 (s, −Me).

Preparation of Gold Phosphites. General Method B. A 10 mL vial was charged in air with the arylgold precursor, secondary phosphite (1 equiv, if it is a solid), and a magnetic stirring bar. The vial was capped, and the atmosphere was exchanged for nitrogen on a manifold. The secondary phosphite (1 equiv, if it is a liquid) was added by syringe along with toluene (8 mL). The reaction was stirred for 18 h at the desired temperature. The volatiles were removed under vacuum, and the gold phosphites were separated from the solid residue by column chromatography. Chromatography details: flash (N_2 pressure), 75 g of basic Al_2O_3 per gram of crude gold phosphite, EtOAc:MeOH (gradient 100:0−90:10). After removal of the volatiles, the residue was dissolved in CH_2Cl_2 and dried over $MgSO_4$. Filtration, concentration, and drying overnight under vacuum afforded the (**5**−**12**) as white solids. If desired, the gold phosphites can be recrystallized by cooling a saturated EtOAc solution to −30 °C.

*Preparation of (JohnPhos)Au(P(O)(OEt)$_2$) (**5**).* The title compound was prepared following general method **B** using (JohnPhos)AuPh (1.000 g, 1.75 mmol) and diethylphosphite (0.225 mL, 1.75 mmol). After heating at 70 °C for 18 h, purification by column chromatography (R_f = 0.22, EtOAc:MeOH 90:10) afforded the title compound as a white solid (1.02 g, 92%).[40]

*Preparation of (^{t}BuXPhos)Au(P(O)(OEt)$_2$) (**6**).* The title compound was prepared following general method **B** using (^{t}BuXPhos)AuPh (1.00 g, 1.43 mmol) and diethylphosphite (0.184 mL, 1.43 mmol). After heating at 70 °C for 18 h, purification by column chromatography (R_f = 0.30, EtOAc:MeOH 90:10) afforded the title compound as a white solid (0.99 g, 91%).[40]

*Preparation of (SIMes)Au(P(O)(OEt)$_2$) (**7**).* The title compound was prepared following general method **B** using (SIMes)AuPh (1.00 g, 1.72 mmol) and diethylphosphite (0.222 mL, 1.72 mmol). After heating at 85 °C for 18 h, purification by column chromatography (R_f = 0.34, EtOAc:MeOH 90:10) afforded the title compound as a white solid (0.91 g, 83%).[40]

*Preparation of (SIPr)Au(P(O)(OEt)$_2$) (**8**).* The title compound was prepared following general method **B** using (SIPr)AuPh (1.00 g, 1.50 mmol) and diethylphosphite (0.194 mL, 1.51 mmol). After heating at 85 °C for 18 h, purification by column chromatography (R_f = 0.36, EtOAc:MeOH 90:10) afforded the title compound as a white solid (0.94 g, 86%). Anal. Calcd for $C_{31}H_{48}AuN_2O_3P$: C, 51.38; H, 6.68. Found: C, 51.59; H, 6.57. ^{1}H ($CDCl_3$, 25 °C): δ 7.38 (t, 2H, J = 7.8, ArH), 7.22 (d, 4H, J = 7.8, ArH), 4.06 (s, 4H, $-NCH_2-$), 3.36 (m, 4H, $-OCH_2-$), 3.03 (sept, 4H, J = 6.8, −CH−), 1.39 (d, 12H, J = 6.8, −Me), 1.33 (d, 12H, J = 6.9, −Me), 0.89 (t, 6H, J = 7.0, −Me). $^{13}C\{^1H\}$ ($CDCl_3$, 25 °C): δ 216.6 (d, J = 168.2, carbene C), 146.8 (s, quat), 133.7 (s, quat), 130.1 (s, ArCH), 124.7 (s, ArCH), 57.1 (s, $-OCH_2-$), 54.0 (d, J = 5.8, $-NCH_2-$), 29.2 (s, −CH−), 25.3 (s, −Me), 24.3 (s, −Me), 16.7 (d, J = 7.8, −Me). $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C): δ 111.6 (s).

*Preparation of (JohnPhos)Au(P(O)Pin) (**9**).* The title compound was prepared following general method **B** using (JohnPhos)AuPh (0.500 g, 0.873 mmol) and HP(O)Pin (0.144 g, 0.877 mmol). After heating at 70 °C for 18 h, purification by column chromatography (R_f = 0.30, EtOAc:MeOH 90:10) afforded the title compound as a white solid (0.49 g, 85%).[40]

*Preparation of (^{t}BuXPhos)Au(P(O)Pin) (**10**).* The title compound was prepared following general method **B** using (^{t}BuXPhos)AuPh (0.500 g, 0.716 mmol) and HP(O)Pin (0.118 g, 0.719 mmol). After heating at 70 °C for 18 h, purification by column chromatography (R_f = 0.41, EtOAc:MeOH 90:10) afforded the title compound as a white solid (0.50 g, 89%).[36]

*Preparation of (SIMes)Au(P(O)Pin) (**11**).* General Method **B** was followed using (SIMes)AuPh (0.500 g, 0.861 mmol) and HP(O)Pin

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(0.142 g, 0.865 mmol). After heating at 85 °C for 18 h, purification by column chromatography (R_f = 0.17, EtOAc:MeOH 95:5) afforded the title compound as a white solid (0.38 g, 66%). Anal. Calcd for $C_{27}H_{38}AuN_2O_3P$: C, 48.65; H, 5.75. Found: C, 48.68; H, 5.59. ^1H ($CDCl_3$, 25 °C): δ 6.92 (s, 4H, ArH), 3.96 (s, 4H, $-NCH_2-$), 2.29 (s, 18H, −Me), 1.24 (s, 6H, −Me), 0.91 (s, 6H, −Me). $^{13}C\{^1H\}$ ($CDCl_3$, 25 °C): δ 214.3 (d, J = 178.0, carbene C), 139.0 (s, quat), 135.6 (s, quat), 134.5 (s, quat), 129.9 (s, ArCH), 83.4 (d, J = 4.6, quat), 51.2 (d, J = 5.8, $-NCH_2-$), 25.3 (d, J = 2.7, −Me), 24.7 (d, J = 5.4, −Me), 21.1 (s, −Me), 18.1 (s, −Me).$^{31}P\{^1H\}$ ($CDCl_3$, 25 °C): δ 120.5 (s).

*Preparation of (SIPr)Au(P(O)Pin) (**12**).* The title compound was prepared following general method **B** using (SIPr)AuPh (0.500 g, 0.752 mmol) and HP(O)Pin (0.124 g, 0.755 mmol). After heating at 85 °C for 18 h, purification by column chromatography (R_f = 0.30, EtOAc:MeOH 95:5) afforded the title compound as a white solid (0.39 g, 69%). Anal. Calcd for $C_{33}H_{50}AuN_2O_3P$: C, 52.80; H, 6.71. Found: C, 52.65; H, 6.59. ^1H ($CDCl_3$, 25 °C): δ 7.39 (t, 2H, J = 7.7, ArH), 7.23 (d, 4H, J = 7.7, ArH), 4.02 (s, 4H, $-NCH_2-$), 3.03 (sept, 4H, J = 6.9, −CH−), 1.42 (d, 12H, J = 6.8, −Me), 1.33 (d, 12H, J = 6.8, −Me), 1.19 (s, 6H, −Me), 0.71 (s, 6H, −Me). $^{13}C\{^1H\}$ ($CDCl_3$, 25 °C): δ 214.5 (d, J = 176.5, carbene C), 146.6 (s, quat), 133.9 (s, quat), 130.2 (s, ArCH), 124.8 (s, ArCH), 83.4 (d, J = 4.8, quat), 54.1 (d, J = 6.1, $-NCH_2-$), 29.2 (s, −CH−), 25.5 (s, −Me), 25.3 (d, J = 2.6, −Me), 24.9 (d, J = 5.3, −Me), 24.2 (s, −Me). $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C): δ 119.0 (s).

Preparation of Vinylgold Compounds: General Method C. A vial (10 mL) was charged (in air) with a gold phosphito compound and a magnetic stirring bar. The atmosphere was exchanged for nitrogen on a vacuum manifold, and DMAD was injected along with toluene. The vial was heated in an aluminum block heater at the desired temperature until consumption of the gold precursor was complete (^{31}P NMR). The volatiles were removed, and the title compound was separated by column chromatography. Chromatography details: flash (N_2 pressure), 50 g of SiO_2 (NEt_3 treated) per gram of crude vinylgold compound, EtOAc:MeOH (gradient 100:0−90:10). After removal of the volatiles, the residue was dissolved in CH_2Cl_2 and dried over $MgSO_4$. Filtration, concentration, and drying overnight under vacuum afforded the vinylgold compounds as waxy solids.

*Preparation of (Z)-(JohnPhos)Au(MeO$_2$C═CO$_2$Me)(P(O)(OEt)$_2$) (**13**).* The title compound was prepared following general method **C** using **5** (1.00 g, 1.58 mmol) and DMAD (0.778 mL, 6.33 mmol, 4 equiv). The reaction mixture was stirred at 80 °C for 48 h. Following purification by column chromatography (R_f = 0.28, hexane:EtOAc 40:60), the title compound was isolated as a pale-yellow wax (1.03 g, 84%). Crystals of **13** that were suitable for X-ray diffraction were grown by cooling a saturated hexane/EtOAc solution (−30 °C). Anal. Calcd for $C_{30}H_{43}AuO_7P_2$: C, 46.52; H, 5.60. Found: C, 46.27; H, 5.81. ^1H ($CDCl_3$, 25 °C): δ 7.87 (t, 1H, J = 7.2, ArH), 7.44 (m 2H, ArH), 7.39 (t, 2H, J = 7.5, ArH), 7.31 (t, 1H, J = 7.4, ArH), 7.23 (m, 1H, ArH), 7.17 (d, 2H, J = 7.5, ArH), 4.08 (m, 4H, $-OCH_2-$), 3.68 (s, 3H, −OMe), 3.67 (s, 3H, −OMe), 1.40 (d, 18H, J = 15.0, −Me), 1.30 (t, 6H, J = 7.1, −Me). $^{13}C\{^1H\}$ ($CDCl_3$, 25 °C): δ 201.8 (dd, J = 95.9, 25.3, quat), 175.5 (d, J = 36.3, quat), 166.4 (dd, J = 23.7, 8.7, quat), 150.5 (d, J = 15.4, quat), 142.0 (d, J = 6.1, quat), 134.6 (s, ArCH), 133.0 (d, J = 7.3, ArCH), 130.2 (d, J = 2.1, ArCH), 129.1 (s, ArCH), 128.9 (s, ArCH), 127.9 (d, J = 200.9, quat), 127.6 (d, J = 36.9, quat), 127.5 (s, ArCH), 126.5 (d, J = 5.6, ArCH), 61.8 (d, J = 5.4, $-OCH_2-$), 51.9 (s, −OMe), 51.0 (s, −OMe), 37.4 (d, J = 21.2, −Me), 30.8 (d, J = 7.1, −Me), 16.5 (d, J = 6.7, −Me). $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C): δ 63.0 (d, J = 14.6, $-PR_3$), 18.8 (d, J = 14.6, $-P(O)(OEt)_2$).

*Preparation of (Z)-(SIMes)Au(MeO$_2$C═CO$_2$Me)(P(O)(OEt)$_2$) (**14**).* The title compound was prepared following general method **C** using **7** (1.00 g, 1.56 mmol) and DMAD (0.768 mL, 6.25 mmol). The reaction mixture was stirred at 80 °C for 48 h. Following purification by column chromatography (R_f = 0.24, 100% EtOAc), the title compound was isolated as a pale-yellow waxy solid (0.93 g, 76%). Crystals of **14** that were suitable for X-ray diffraction were grown by cooling the crude reaction mixture (0 °C). Anal. Calcd for $C_{31}H_{42}AuN_2O_7P$: C, 47.58; H, 5.41. Found: C, 47.32; H, 5.41. ^1H ($CDCl_3$, 25 °C): δ 6.94 (s, 4H, ArH), 3.94 (s, 4H, $-NCH_2-$), 3.72 (m, 4H, $-OCH_2-$), 3.59 (s, 3H, −OMe), 3.47 (s, 3H, −OMe), 2.33 (s, 12H, −Me), 2.29 (s, 6H, −Me), 1.10 (t, 6H, J = 7.0, −Me). $^{13}C\{^1H\}$ ($CDCl_3$, 25 °C): δ 209.7 (d, J = 5.2, carbene C), 195.3 (d, J = 23.6, quat), 176.2 (d, J = 35.6, quat), 166.5 (d, J = 24.3, quat), 138.6 (s, quat), 136.0 (s, quat), 135.0 (s, quat), 129.6 (s, ArCH), 129.2 (d, J = 196.2, quat), 61.9 (d, J = 5.2, $-OCH_2-$), 51.8 s, −OMe), 51.1 (s, $-CH_2N-$), 21.2 (s, −Me), 18.1 (s, −Me), 16.5 (d, J = 6.2, −Me). $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C): δ 18.3 (s).

*Preparation of (S$_p$)-(SIMes)Au(P(O)Ph((−)O-Men)) (**15**).* The title compound was prepared following general method **B** using **7** (1.000 g, 1.72 mmol) and (R_p)-HP(O)Ph((−)O-Men) (0.483 g, 1.72 mmol, dr > 90:1). After stirring at 100 °C for 24 h, the title compound was isolated by column chromatography (R_f = 0.34, EtOAc:MeOH 95:5) as a white solid (0.98 g, 73%, dr > 90:1). Anal. Calcd for $C_{37}H_{50}AuN_2O_2P$: C, 56.77; H, 6.44. Found: C, 56.40; H, 6.06. ^1H ($CDCl_3$, 25 °C): δ 7.26 (dd, 2H, J = 12.7, 7.5, o-C_6H_5), 7.20 (t, 1H, J = 7.4, p-C_6H_5), 7.13 (t, 2H, J = 7.5, m-C_6H_5), 6.97 (s, 2H, ArH), 6.92 (s, 2H, ArH), 4.00 (s, 4H, $-NCH_2-$), 3.74 (m, 1H, −OCH−), 2.34 (s, 6H, −Me), 2.31 (s, 6H, −Me), 2.30 (s, 6H, −Me), 2.22 (m, 1H, $-CH_2-$), 1.84 (septd, 1H, J = 7.0, 2.9, −CH−), 1.53 (m, 2H, $-CH_2-$), 1.19 (m, 1H, −CH−), 1.07 (m, 2H, −CH−, $-CH_2-$), 0.82 (d, 3H, J = 6.0, -Me), 0.76 (m, 2H, $-CH_2-$), 0.72 (d, 3H, J = 7.0, −Me), 0.59 (d, 3H, J = 7.0, −Me). $^{13}C\{^1H\}$ ($CDCl_3$, 25 °C): δ 217.5 (d, J = 143.0, carbene C), 146.4 (d, J = 73.9, quat), 139.1 (s, quat), 135.8 (s, quat), 135.7 (s, quat), 134.5 (s, quat), 129.90 (s, ArCH), 129.85 (s, ArCH), 129.76 (d, J = 16.6, ArCH), 128.9 (d, J = 1.9, ArCH), 127.4 (d, J = 11.6, ArCH), 78.3 (s, −OCH−), 51.3 (d, J = 4.8, $-NCH_2-$), 48.7 (d, J = 8.7, −CH−), 44.3 (s, $-CH_2-$), 34.7 (s, $-CH_2-$), 31.8 (s, −CH−), 24.5 (s, −CH−), 23.4 (s, $-CH_2-$), 22.1 (s, −Me), 21.2 (s, −Me), 21.0 (s, −Me), 18.2 (s, −Me), 18.1 (s, −Me), 16.8 (s, −Me). $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C): δ 119.1 (s).

*Preparation of (S$_p$)-(JohnPhos)Au(P(O)Ph((−)O-Men)) (**16**).* The title compound was prepared following general method **B** using **5** (1.00 g, 1.75 mmol) and (R_p)-HP(O)Ph((−)O-Men) (0.490 g, 1.75 mmol, dr > 90:1). After stirring at 115 °C for 18 h, the title compound was isolated by column chromatography (R_f = 0.46, EtOAc:MeOH 90:10) as a white solid (1.16 g, 86%, dr > 90:1).[36]

*Preparation of (Z)-(JohnPhos)Au(MeO$_2$C═CO$_2$Me)(P(O)Ph(O-Men)) (**17**).* The title compound was prepared following general method **C** using **16** (0.500 g, 0.645 mmol) and DMAD (0.317 mL, 2.58 mmol, 4 equiv). After stirring at 80 °C for 48 h, the title compound was isolated by column chromatography (R_f = 0.44, EtOAc:hexane 70:30) as a white waxy solid (0.26 g, 44%, dr > 90:1). Anal. Calcd for $C_{42}H_{57}AuO_6P_2$: C, 55.02; H, 6.27. Found: C, 54.54; H, 6.26. ^1H ($CDCl_3$, 25 °C): δ 7.90 (m, 3H, ArH), 7.43 (m, 6H, ArH), 7.29 (m, 1H, ArH), 7.22 (m, 1H, ArH), 7.16 (br d, 1H, J = 7.6 ArH), 7.10 (m, 2H, ArH), 4.22 (m, 1H, −CH−), 3.67 (s, 3H, −OMe), 3.49 (s, 3H, −OMe), 2.20 (m, 1H, $-CH_2-$), 2.12 (dsept, 1H, J = 7.0, 1.9, −CH−), 1.61 (m, 2H, $-CH_2-$), 1.46 (d, 9H, J = 15.0, −Me), 1.39 (d, 9H, J = 14.8, −Me), 1.35 (m, 2H, −CH−), 1.14 (m, 1H, $-CH_2-$), 0.95 (m, 1H, $-CH_2-$), 0.86 (d, 3H, J = 7.1, −Me), 0.83 (m, 1H, $-CH_2-$), 0.81 (d, 3H, J = 6.5, −Me), 0.74 (d, 3H, J = 6.9, −Me). $^{13}C\{^1H\}$ ($CDCl_3$, 25 °C): δ 202.6 (dd, J = 95.7, 23.6, quat), 176.2 (d, J = 31.2, quat), 166.4 (dd, J = 23.0, 9.0, quat), 150.6 (d, J = 15.4, quat), 141.9 (d, J = 6.3, quat), 136.1 (d, J = 141.5, quat), 134.6 (s, ArCH), 133.0 (d, J = 7.1, ArCH), 131.5 (d, J = 10.4, ArCH), 131.1 (d, J = 145.9, quat), 130.9 (d, J = 2.9, ArCH), 130.1 (d, J = 2.1, ArCH), 129.2 (s, ArCH), 129.1 (s, ArCH), 128.9 (s, ArCH), 128.7 (s, ArCH), 127.8 (d, J = 36.2, quat), 127.7 (d, J = 13.3, ArCH), 127.4 (s, ArCH), 126.5 (d, J = 5.5, ArCH), 76.4 (d, J = 7.1, −CH−), 51.3 (s, −OMe), 50.9 (s, −OMe), 48.9 (d, J = 6.6, −CH−), 43.8 (s, $-CH_2-$), 37.5 (d, J = 21.3, quat), 37.4 (d, J = 20.6, quat), 34.4 (s, $-CH_2-$), 31.8 (s, −CH−), 30.9 (d, J = 7.1, −Me), 25.2 (s, −CH−), 22.9 (s, $-CH_2-$), 22.1 (s, −Me), 21.4 (s, −Me), 15.8 (s, −Me). $^{31}P\{^1H\}$ ($CDCl_3$, 25 °C): δ 63.6 (d, J = 12.3, $-PR_3$), 29.0 (d, J = 12.3, −P(O)−).

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*Preparation of (Z)-(MeO$_2$C)(I)C═C(CO$_2$Me)(P(O)(OEt)$_2$) (**18**).* A vial (10 mL) was charged with **13** (1.00 g, 1.29 mmol), iodine (0.328 g, 1.29 mmol), and a stirring bar. The atmosphere was exchanged for nitrogen, and toluene (5 mL) was injected by syringe. After stirring (12 h, 25 °C), the volatiles were removed under vacuum, and the residue was dissolved in a minimal amount of hot ethyl acetate. The solution was filtered through Celite and allowed to cool to room temperature. Crystals of JohnPhosAuI formed after 24 h and were separated. The ethyl acetate was evaporated, and the title compound was isolated by column chromatography (R_f = 0.67, EtOAc) as a light tan oil (0.48 g, 89%). A small amount of JohnPhosAuI was also isolated from the column, and combining the two JohPhosAuI samples afforded 0.75 g (93%) of the iodogold compound. Anal. Calcd for $C_{10}H_{16}IO_7P$: C, 29.58; H, 3.97. Found: C, 29.58; H, 4.17. ^{1}H ($CDCl_3$, 25 °C): δ 4.22 (m, 4H, −CH_2−), 3.83 (s, 3H, −OMe), 3.82 (s, 3H, −OMe), 1.37 (t, 6H, J = 7.1, −Me). ^{13}C{^{1}H} ($CDCl_3$, 25 °C): δ 165.2 (d, J = 10.4, C═O), 164.1 (d, J = 22.7, C═O), 143.2 (d, J = 180.9, quat), 105.6 (s, quat), 64.0 (d, J = 5.8, −OCH_2−), 54.3 (s, −OMe), 53.4 (s, −OMe), 16.4 (d, J = 6.5, −Me). ^{31}P{^{1}H} ($CDCl_3$, 25 °C): δ 7.0 (s).

Preparation of Alkynylgold Compounds. General Method D. A vial (10 mL) was charged with a gold phosphito precursor and a magnetic stirring bar. The vial was capped, and the atmosphere was exchanged for nitrogen. Methyl propiolate (5 equiv) was injected by syringe along with toluene (6 mL). After the reaction was complete, the volatiles were removed, and the title compound was purified by column chromatography. Chromatography details: flash (N_2 pressure), 25 g of NEt_3 treated SiO_2 per gram of crude alkynylgold compound, hexane:EtOAc (gradient 100:0−30:70). After removal of the volatiles, the residue was dissolved in CH_2Cl_2 and dried over $MgSO_4$. Filtration, concentration, and drying overnight under vacuum afforded the alkynylgold compounds as white solids. If desired, the alkynylgold compounds can be recrystallized by cooling a saturated hexane/EtOAc solution to −30 °C.

*Preparation of (JohnPhos)Au(C≡CCO$_2$Me) (**19**).* The title compound was prepared following general method **D** using (**5**) (1.00 g, 1.58 mmol) and methyl propiolate (0.703 mL, 7.91 mmol, 5 equiv). After heating at 70 °C for 18 h, purification by column chromatography (R_f = 0.37, hexane:EtOAc 70:30) afforded the title compound as a white solid (0.66 g, 72%). Anal. Calcd for $C_{24}H_{30}AuO_2P$: C, 49.83; H, 5.23. Found: C, 49.93; H, 5.19. ^{1}H ($CDCl_3$, 25 °C): δ 7.83 (t, 1H, J = 3.9, ArH), 7.48 (m, 5H, ArH), 7.27 (m, 1H, ArH), 7.11 (d, 2H, J = 7.6, ArH), 3.69 (s, 3H, −OMe), 1.37 (d, 18H, J = 15.0, −Me). ^{13}C{^{1}H} ($CDCl_3$, 25 °C): δ 154.4 (d, J = 2.9, quat), 150.3 (d, J = 15.0, quat), 142.2 (d, J = 6.2, quat), 138.2 (d, J = 129.4, quat), 134.3 (d, J = 1.0, ArCH), 133.1 (d, J = 7.1, ArCH), 130.5 (d, J = 2.3, ArCH), 129.2 (s, ArCH), 129.1 (s, ArCH), 128.4 (s, ArCH), 127.0 (d, J = 41.3, quat), 126.8 (d, J = 6.2, ArCH), 91.9 (d, J = 22.0, quat), 51.9 (s, −OMe), 37.6 (d, J = 22.7, -quat), 31.0 (d, J = 6.9, −Me). ^{31}P{^{1}H} ($CDCl_3$, 25 °C): δ 64.0 (s).

*Preparation of (^{t}BuXPhos)Au(C≡CCO$_2$Me) (**20**).* The title compound was prepared following general method **D** using (**6**) (0.423 g, 0.558 mmol) and methyl propiolate (0.248 mL, 2.79 mmol, 5 equiv). After heating at 70 °C for 18 h, purification by column chromatography (R_f = 0.86, hexane:EtOAc 70:30) afforded the title compound as a white solid (0.32 g, 81%). Anal. Calcd for $C_{33}H_{48}AuO_2P$: C, 56.25; H, 6.87. Found: C, 55.94; H, 6.81. ^{1}H ($CDCl_3$, 25 °C): δ 7.85 (td, 1H, J = 7.6, 1.2, ArH), 7.46 (m, 2H, ArH), 7.30 (ddd, 1H, J = 7.6, 4.6, 1.5, ArH), 7.12 (s, 2H, ArH), 3.67 (s, 3H, -OMe), 3.02 (sept, 1H, J = 6.9, −CH−), 2.33 (sept, 1H, J = 6.7, −CH−), 1.40 (d, 18H, J = 15.0, −Me), 1.35 (d, 6H, J = 6.9, −Me), 1.30 (d, 6H, J = 6.8, −Me), 0.91 (d, 6H, J = 6.6, −Me). ^{13}C{^{1}H} ($CDCl_3$, 25 °C): δ 154.4 (d, J = 2.9, quat), 149.9 (s, quat), 148.6 (d, J = 15.5, quat), 145.8 (s, quat), 139.1 (d, J = 129.8, quat), 135.6 (d, J = 5.2, quat), 135.3 (d, J = 1.7, ArCH), 134.8 (d, J = 7.9, ArCH), 130.1 (d, J = 2.0, ArCH), 129.2 (d, J = 38.6, quat), 126.5 (d, J = 6.2, ArCH), 122.2 (s, ArCH), 91.7 (d, J = 22.5, quat), 51.8 (s, −OMe), 38.2 (d, J = 23.6, quat), 33.9 (s, −Me), 31.5 (d, J = 6.7, −Me), 31.0 (s, −CH−), 26.4 (s, −Me), 24.0 (s, −Me), 23.2 (s, −Me). ^{31}P{^{1}H} ($CDCl_3$, 25 °C): δ 63.4 (s).

*Preparation of (SIMes)Au(C≡CCO$_2$Me) (**21**).* The title compound was prepared following general method **D** using (**7**) (0.500 g, 0.781 mmol) and methyl propiolate (0.347 mL, 3.90 mmol, 5 equiv). After heating at 85 °C for 18 h, purification by column chromatography (R_f = 0.28, hexane:EtOAc 70:30) afforded the title compound as a white solid (0.32 g, 70%).[40]

*Preparation of (SIPr)Au(C≡CCO$_2$Me) (**22**).* The title compound was prepared following general method **D** using (**8**) (0.630 g, 0.869 mmol) and methyl propiolate (0.387 mL, 4.35 mmol, 5 equiv). After heating at 85 °C for 18 h, purification by column chromatography (R_f = 0.39, hexane:EtOAc 70:30) afforded the title compound as a white solid (0.46 g, 79%). Anal. Calcd for $C_{31}H_{41}AuN_2O_2$: C, 55.52; H, 6.16. Found: C, 55.47; H, 6.06. ^{1}H ($CDCl_3$, 25 °C): δ 7.41 (t, 2H, J = 7.7, ArH), 7.23 (d, 4H, J = 7.7, ArH), 4.01 (s, 4H, −NCH_2−), 3.57 (s, 3H, −OMe), 3.03 (sept, 4H, J = 6.8, −CH−), 1.40 (d, 12H, J = 6.8, −Me), 1.33 (d, 12H, J = 6.9, −Me). ^{13}C{^{1}H} ($CDCl_3$, 25 °C): δ 209.6 (s, carbene C), 154.1 (s, quat), 146.7 (s, quat), 134.02 (s, quat), 133.95 (s, quat), 130.1 (s, ArCH), 124.7 (s, ArCH), 93.3 (s, quat), 53.9 (s, −NCH_2−), 51.9 (s, −OMe), 29.1 (s, −CH−), 25.4 (s, −Me), 24.2 (s, −Me).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.1c00283.

NMR spectra of all new compounds (PDF)

Accession Codes

CCDC 2080845−2080850 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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