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Efficient Cycloisomerization of Propargyl Amides by Electrophilic Gold(I) Complexes of KITPHOS Monophosphines: A Comparative Study

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Electrophilic gold(I) complexes of diphenyl- and dicyclohexylphosphino-based KITPHOS monophosphines catalyze the 5-exo-dig cycloisomerization of a range of propargyl amides to afford the corresponding alkylidene oxazolines; in all cases catalysts formed from diphenylphosphino-substituted KITPHOS monophosphines outperformed their dicyclohexylphosphino counterparts as well as that based on triphenylphosphine, an indication that the biaryl/biaryl-like framework may be responsible for imparting high catalyst efficiency.

Introduction

The catalytic activation of carbon−carbon π-bonds by carbophilic Lewis acid complexes of gold(I) and gold(III) has evolved into an extremely powerful tool for the construction of diverse and complex mono- and polycylic architectures.[1] In the vast majority of these transformations an alkyne is activated toward nucleophilic addition by coordination to an electrophilic gold complex; the fate of such complexes includes intramolecular carbocyclizations, skeletal rearrangements, inter- and intramolecular addition of X−H bonds (X = O, N, S), and cyclizations initiated by addition of weak nucleophiles such as a carbonyl oxygen atom.[2] In many cases, phosphines and N-heterocyclic carbenes are proving to be the ligands of choice for gold(I)-catalyzed transformations, and there is increasing evidence that both reactivity and selectivity depend on the steric and/or electronic properties of the supporting ligand.[3] For example, Asensio has reported that the gold(I)-catalyzed cyclization of 3-substituted 1-(*o*-ethynylaryl)ureas occurs via either a 6-exo-dig or 5-endo-dig pathway depending on the choice of ligand, with bulky N-heterocyclic carbenes giving high 6-exo-dig selectivity,[4] and Toste has demonstrated that the stability of gold(I) carbene intermediates can be modulated by adjusting the electronic properties of the supporting ligand; in this case an electron-rich biaryl monophosphine provided the optimum combination of electronic and steric properties.[5] In this regard, although electron-rich biaryl monophosphines have had their greatest impact on palladium-catalyzed cross-coupling,[6] they are rapidly emerging as highly successful/efficient ligands for a host of gold(I)- and gold(III)-catalyzed transformations.[7]

We have recently developed an architecturally related class of electron-rich biaryl-like monophosphines, KITPHOS

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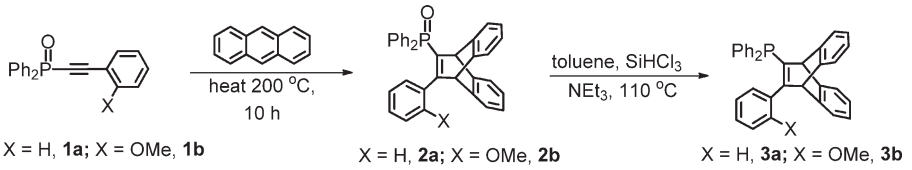
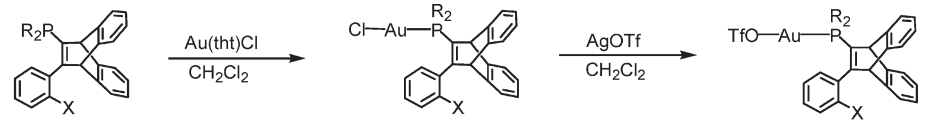
Scheme 1



X = H, **1a;** X = OMe, **1b** X = H, **2a;** X = OMe, **2b** X = H, **3a;** X = OMe, **3b**

Scheme 2



R = Ph; X = H, **3a;** X = OMe, **3b**
R = Cy; X = H, **3c**; X = OMe, **3d**

R = Ph; X = H, **4a;** X = OMe, **4b**
R = Cy; X = H, **4c**; X = OMe, **4d**

R = Cy; X = OMe, **5**

(11-dicyclohexylphosphino-12-phenyl-9,1-ethenoanthracenes), which also form highly efficient catalysts for C−C and C−N cross-coupling of a range of aryl chlorides.[8] The similarity between the basic skeletal framework of KITPHOS monophosphines and Buchwald's electron-rich biaryl monophosphines coupled with their competitive performance in palladium-catalyzed cross-coupling prompted us to explore their efficiency in gold-catalyzed cyclizations.[9] Our preliminary studies were encouraging as electrophilic Lewis acid gold(I) complexes of the corresponding electron-rich KITPHOS monophosphines efficiently catalyzed a range of intramolecular cyclizations to afford phenols, tetrahydropyrans, lactones, and alkylidene oxazolines; in the majority of cases these catalysts were superior to those previously reported. Having restricted our initial study to electron-rich KITPHOS monophosphines, we subsequently initiated a systematic comparison between their PPh_2- and PCy_2-based counterparts with the aim of beginning to establish what factors control catalyst performance. In this regard, PPh_2-based biaryl monophosphines have received much less attention than their PCy_2 and P^tBu_2 analogues on the basis that they are less electron rich and lack steric bulk, requirements commonly accepted to be necessary for efficient platinum group metal catalyzed C−C and C−N bond formation.[10] The cycloisomerization of propargyl amides was selected as the benchmark reaction for this study since these substrates are easily accessible in a single step[11] and the resulting alkylidene oxazoline is a potentially useful intermediate, while its isomeric oxazole counterpart is a substructure of a number of naturally occurring products and bioactive compounds;[12] both products can be selectively prepared using gold(I)- and gold(III)-based catalysts, respectively.[13] Herein we disclose the results of this study, which has conclusively shown that catalysts based on diphenylphosphino-containing KITPHOS monophosphines outperform their dicyclohexylphosphino counterparts and that the former are markedly more efficient than $[Au(PPh_3)]^+$,[13b] with the corollary that the biaryl fragment appears be necessary for efficient catalysis; cationic gold(I) complexes containing a KITPHOS monophosphine and a thioether have also been shown to be practical and highly efficient precatalysts.

Results and Discussion

Ligand Synthesis and Coordination Chemistry. KITPHOS monophosphines **3a**,**b** required for this study were prepared in good yield following the procedure previously reported for their dicyclohexylphosphino counterparts **3c**,**d**,[8] which involved the Diels−Alder cycloaddition between 1-alkynyl phosphine oxides **1a**,**b** and anthracene to construct the bicyclic framework followed by reduction of the resulting KITPHOS monoxide **2a**,**b** with chlorosilane/triethylamine in toluene (Scheme 1). The identity and purity of **3a**,**b** have been established using conventional spectroscopic and analytical techniques.

With the intention of undertaking comparative testing of KITPHOS monophosphines **3a**−**d** in the gold(I)-catalyzed cycloisomerization of a range of propargyl amides, precursors **4a**−**d** were prepared by reaction of [(tht)AuCl][14] with the corresponding KITPHOS monophosphine in dichloromethane (Scheme 2). As relatively few gold(I) complexes of KITPHOS monophosphines have been crystallographically characterized,[9] single-crystal X-ray analyses of **4b** and **4d** were undertaken to compare their key structural features; perspective views of the molecular structures are shown in Figures 1 and 2, respectively.

Figures 1 and 2 show that the gold atoms in **4b** and **4d** adopt a near-linear geometry with P(1)−Au(1)−Cl(1) bond angles of 176.31(4)° and 178.09(3)°, respectively, well within

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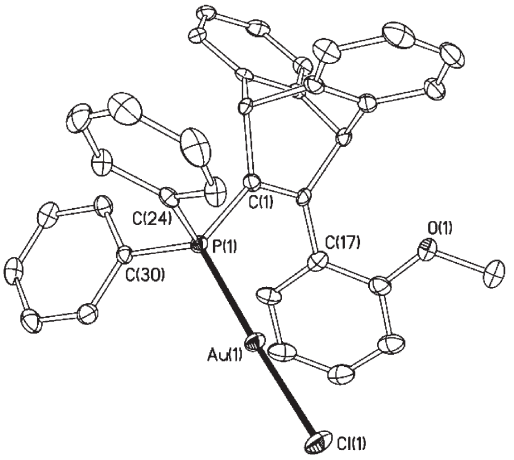

Figure 1. Molecular structure of [{11-(diphenylphosphino)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene}-AuCl] (**4b**). Hydrogen atoms and the dichloromethane molecule of crystallization have been omitted for clarity. Ellipsoids are at the 40% probability level.

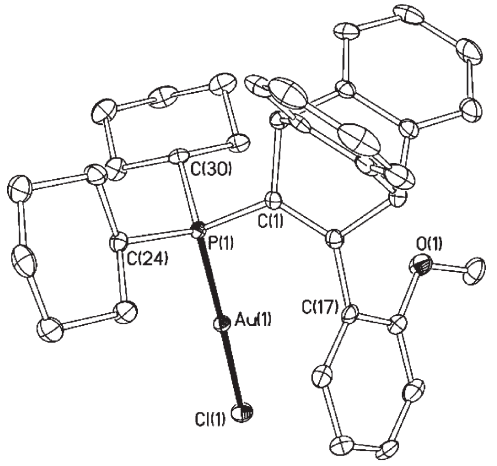

Figure 2. Molecular structure of [{11-(dicyclohexylphosphino)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene}AuCl] (**4d**). Hydrogen atoms and the dichloromethane molecule of crystallization have been omitted for clarity. Ellipsoids are at the 40% probability level.

the range reported for related complexes.[15] The Au(1)−Cl(1) bond length of 2.2794(11) Å in **4b** is slightly shorter than that of 2.2935(7) Å in **4d**, which most likely reflects the different *trans* influence of the dicyclohexylphosphino group compared with its diphenylphosphino counterpart. The Au(1)−P(1) bond length of 2.2348(7) Å in **4d** is comparable to those reported for gold(I) complexes of electron-rich biaryl monophosphines such as [{PCy_2(*o*-biphenyl)}AuCl] (2.2364(6) Å),[15] [{PCy_2(2′,6′-dimethoxybiphenyl)}AuCl] (2.2378(5) Å),[15] and [{PCy_2(2′,4′,6′-triisopropylbiphenyl)}AuCl] (2.2349(11) Å),[16] whereas the corresponding bond length of 2.2188(9) Å in **4b** is markedly shorter and is among the shortest 5% of over 6000 Au−P bonds recorded in the Cambridge Structural Database.[17] There is a weak η^1-interaction between the gold atom and the *ipso* carbon atom of the anisyl ring in **4d**; the Au(1)···C(17) distance of 3.150 Å is less than the sum of the van der Waals radii of gold and carbon and similar to the Au···C_{ipso} interactions reported for gold(I) chloride complexes of PCy_2(*o*-biphenyl) and PBu^t_2(*o*-biphenyl).[15,16,18] In stark contrast, even though the anisyl ring in diphenylphosphino-based **4b** adopts a similar orientation with respect to the Au−P bond, the corresponding Au···C_{ipso} distance of 3.367 Å is significantly longer and well outside the range defined by the sum of the van der Waals radii. The Au(1)−O(1) distances of 4.411 and 4.066 Å in **4b** and **4d**, respectively, are markedly longer than that of 3.27 Å in [{PCy_2(2′,6′-dimethoxybiphenyl)}AuCl]. In this regard, a weak interaction between palladium and the oxygen atom of a methoxy group on the non-phosphine-containing aryl ring of electron-rich biaryl monophosphines has been suggested to contribute to the stability and hence efficiency of Pd/SPHOS-based catalysts, and as such, the structures of a number of Pd(0) and Pd(II) complexes of this ligand have been determined; Pd−O interactions as short as 2.973 Å have been identified.[19]

Although it is operationally straightforward to generate electrophilic gold(I) catalysts by abstraction of chloride with a silver salt of a noncoordinating anion immediately prior to the addition of substrate, it has recently become common practice to isolate cationic complexes, as they are generally robust and air-stable, which means they can be prepared on a large scale, stored, and used directly, thus avoiding the use of cocatalysts that are hygroscopic and difficult to weigh accurately on a small scale.[20] With the intention of comparing the efficiency of catalyst generated *in situ* with the corresponding isolated complex, cation **5** was generated by reaction of **4d** with AgOTf in dichloromethane, isolated, and characterized by a single-crystal X-ray study; the molecular structure is shown in Figure 3. The geometry about the gold is close to linear, with a P(1)−Au(1)−O(2) bond angle of 175.52(10)°. The Au(1)−P(1) bond length of 2.2112(11) Å is shorter than those in related cationic complexes such as [{PCy_2(*o*-biphenyl)}Au(MeCN)][SbF_6] (2.2466(3) Å)[15] and [{PBu^t_2(*o*-biphenyl)}Au(MeCN)][SbF_6] (2.2539(7) Å)[15] as well as that of 2.2244(10) Å in the bis(trifluoromethane)-sulfonimide complex of the same KITPHOS monophosphine.[9] The anisyl ring in **5** also adopts an orientation similar to that in **4d** such that it is in close proximity to the gold atom; the Au···C_{ipso} distance of 3.147 Å is essentially the same as the corresponding distance in **4d**.

Complexes of the type [(R_3P)AuL]X, which contain a neutral weakly coordinating ligand L such as a nitrile, have also been used as precursors for a host of gold(I)-catalyzed skeletal rearrangements and transformations.[21] In contrast,

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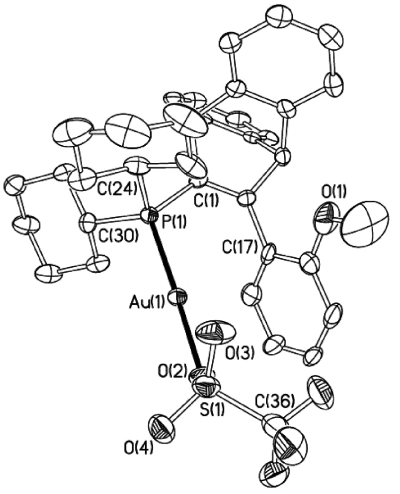
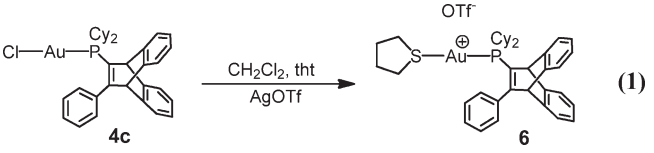


Figure 3. Molecular structure of one of the two independent molecules of [{11-(dicyclohexylphosphino)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene}Au(SO_3CF_3)] (**5**). Hydrogen atoms have been omitted for clarity. Ellipsoids are at the 40% probability level.

there are very few reports of gold(I) complexes that contain both a phosphine and a thioether and none that describe their use in catalysis.[22] Since we were interested in exploring whether gold(I) complexes of tetrahydrothiophene (tht), or indeed other thioethers could be an alternative class of catalyst precursor, a dichloromethane solution of **4c**, generated in situ by reaction of **3c** with Au(tht)Cl in the presence of a slight excess of tht, was treated with one equivalent of silver triflate to give **6** in near-quantitative yield (eq 1). We note here that our initial rationale for preparing **6** was the low solubility of **4c** in all common chlorinated and non-chlorinated solvents; we reasoned that, as a cation, **6** would be more soluble, easier to purify, and therefore a more practical precatalyst, provided that the tetrahydrothiophene is weakly coordinated and does not affect catalyst efficiency (*vide infra*). As **6** is the first example of a gold(I) complex supported by an electron-rich biaryl monophosphine and a thioether,[23] a single-crystal X-ray study was undertaken to compare the key geometrical features with those of **4d** and **5**. Figure 4 clearly shows that the phenyl ring is orientated parallel to the Au−P bond; however, the Au(1)···C(17) distance of 3.283 Å is markedly longer than that of 3.150 and 3.147 Å in **4d** and **5**, respectively. The gold atom in **6** has a near-linear geometry, with a P(1)−Au(1)−S(1) bond angle of 175.60(7)°; for comparison the corresponding bond angles in [(PPh_3)Au(SMe_2)][OTf][22b] and [{PPh_2(*o*-$C_6H_4NH_2$)}Au(tht)]-[ClO_4][22c] are 172.98° and 179.20°, respectively.



(1)

Having already demonstrated that KITPHOS monophosphines **4c**,**d** are effective ligands for gold-catalyzed intra-

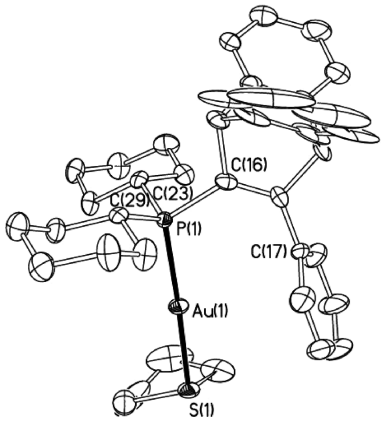


Figure 4. Molecular structure of [{2-(dicyclohexylphosphino)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene}Au(tht)][SO_3CF_3] (**6**). Hydrogen atoms, the chloroform molecule of crystallization, and the trifluoromethanesulfonate anion have been omitted for clarity. Ellipsoids are at the 40% probability level.

molecular cyclizations, we chose the cycloisomerization of propargyl amides[13] from our initial study to systematically compare the performance of diphenylphosphine-based KITPHOS monophosphines **3a**,**b** against their dicyclohexylphosphine-based counterparts **3c**,**d**, full details of which are listed in Table 1. Our preliminary comparison focused on cycloisomerization of the *tert*-butyl-based propargyl amide **7a** in dichloromethane using 2 mol % catalyst generated from **4a**−**d** and silver triflate. Under these conditions each of the catalysts gave excellent conversion to the corresponding methylene oxazoline **8a** with no evidence for the formation of its oxazole counterpart; this is entirely consistent with recent studies that have firmly established that Au(I)-based catalysts are selective for the formation of the methyleneoxazoline, while Au(III) systems afford the corresponding oxazole.[13b,24] As near-quantitative conversions were obtained for each catalyst, the comparison was extended to include a range of alkyl-, aryl-, and heteroraryl-substituted substrates, with the aim of revealing any differences in performance. While each catalyst gave good to excellent conversions for all substrates tested, those based on **3a**,**b** consistently outperformed their dicyclohexylphosphino counterparts. The difference in performance between systems based on **3a**,**b** and **3c**,**d** manifests itself most evidently in the cycloisomerization of the cyclohexyl- and phenyl-containing propargyl amides, **7b** and **7c**, respectively. For example, 2 mol % **4b**/AgOTf catalyzed cycloisomerization of the phenyl substrate to give 85% conversion after 1.5 h compared with only 51% conversion for **4d**/AgOTf in the same time. This trend in catalyst efficiency also extended to the heteroaromatic propargyl amides, although longer reaction times were required for each substrate to reach acceptable conversions. For comparison, the **4b**/AgOTf-catalyzed cycloisomerization of thienyl substrate

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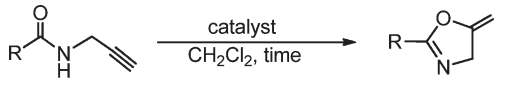
(23) For an example of a gold(I) complex of a triethylphosphine and tetrahydrothiophene see: El-Etri, M. M.; Scovell, W. M. *Inorg. Chem.* **1990**, *29*, 480.

(24) The gold(I)-catalyzed intramolecular hydroamination of propargyl alcohol-derived trichloroacetimidates selectively affords the methylene dihydrooxazole with no evidence for the corresponding oxazole. Kang, J.-E.; Kim, H.-B.; Lee, J.-W.; Shin, S. *Org. Lett.* **2006**, *8*, 3537.

Table 1. Gold(I)-Catalyzed Cycloisomerization of Propargyl Amides 7a−f



7a-f **8a-f**

Entry	substrate	Catalyst	mol %	Time (h)	% Conversion[f]
1[a]		**4a**	2	1	96
2[a]		**4b**	2	1	>99
3[a]		**4c**	2	1	92
4[a]		**4d**	2	1	97
5[b]	**7a**	**5**	2	1	>99
6[c]		**6**	2	1	95
7[a]		**4a**	2	1.5	84
8[a]		**4b**	2	1.5	85
9[a]		**4c**	2	1.5	63
10[a]		**4d**	2	1.5	51
11[b]	**7b**	**5**	2	1.5	58
12[c]		**6**	2	1.5	58
13[a]		**4a**	2	0.5	74
14[a]		**4b**	2	0.5	74
15[a]		**4c**	2	0.5	61
16[a]		**4d**	2	0.5	45
17[b]	**7c**	**5**	2	0.5	46
18[c]		**6**	2	0.5	65
19[e]		**[Au(PPh$_3$)]NTf$_2$**	1	36	79
20[a]		**4a**	2	4	79
21[a]		**4b**	2	4	84
22[a]		**4c**	2	4	57
23[a]		**4d**	2	4	59
24[b]	**7d**	**5**	2	4	61
25[c]		**6**	2	4	64
26[a,d]		**4a**	2	5	80
27[a,d]		**4b**	2	5	93
28[a,d]		**4c**	2	5	69
29[a,d]		**4d**	2	5	61
30[b,d]	**7e**	**5**	2	5	87
31[c,d]		**6**	2	5	65
32[e]		**[Au(PPh$_3$)]NTf$_2$**	5	24	67
33[a]		**4a**	2	1.5	85
34[a]		**4b**	2	1.5	87
35[a]		**4c**	2	1.5	73
36[a]		**4d**	2	1.5	71
37[b]	**7f**	**5**	2	1.5	76
38[c]		**6**	2	1.5	77
39[e]		**[Au(PPh$_3$)]NTf$_2$**	1	36	91

[a] Reaction conditions: (i) 2 mol % **4a**−**d**, 2 mol % AgOTf, CH_2Cl_2, stir 30 min, (ii) 0.5 mmol propargyl amide, room temperature. [b] Reaction conditions: (i) 2 mol % isolated **5**, 0.5 mmol propargyl amide, CH_2Cl_2, room temperature. [c] Reaction conditions: (i) 2 mol % isolated **6**, 0.5 mmol propargyl amide, CH_2Cl_2, room temperature. [d] Reaction conducted in 1,2-dichloroethane at 50 °C. [e] See ref 13d for full experimental details. [f] Conversions determined by ^{1}H NMR analysis of the reaction mixture. Average of two runs.

7d reached 84% conversion after 4 h, whereas its furyl counterpart **7e** required heating at 50 °C for 5 h to achieve a similar conversion; the corresponding dicyclohexylphosphino-based catalysts gave 59% and 61% conversion, respectively. Finally, while **4a-b**/AgOTf and **4c-d**/AgOTf both gave good conversions of cinnamyl-based substrate **7f** to methylene oxazoline **8f**, the former pair was consistently more efficient, albeit only marginally. Reassuringly, there is an extremely close correlation between the performance of catalyst generated by activation of **4d** with silver triflate and its isolated cation **5**. As a slight excess of cocatalyst is typically used to ensure quantitative activation of the precatalyst and Lewis acid silver salts have been shown to activate alkynes toward cyclization,[25] parallel control experiments were conducted for each substrate tested using 2 mol % AgOTf in the absence of **4a**−**d**. Although these experiments conclusively showed that AgOTf is not an active cycloisomerization catalyst for propargyl amides,[26] they do not exclude a

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(26) Silver salts such as $AgNO_3$ and $AgSbF_6$ have been reported to catalyze the cycloisomerization of *N*-propargylamides; however, substrates lacking *gem*-dialkyl substitution showed no reaction in dichloromethane. Harmata, M.; Huang, C. *Synlett* **2008**, 1399.

more subtle role for adventitious Ag^+ such as interception of Au(I) intermediates, as recently described by Gagné and co-workers.[27] Gratifyingly, the mixed phosphine−tetrahydrothiophene cation **6** gave conversions that matched those obtained with the corresponding system generated from **4c**. Thus, even though **6** was initially prepared to overcome the low solubility of precatalyst **4c**, it appears that cationic gold(I)-phosphine complexes of tetrahydrothiophene may prove to be an alternative, practical, and highly efficient class of precatalyst that are air-stable as well as easy to prepare and handle.

In an extension to our description of **3c**,**d** as electron-rich biaryl-like monophosphines, considering **3a**,**b** as architectural analogues of the corresponding triarylphosphines prompted us to compare the efficiency of Au(I)/**3a** against $[Au(PPh_3)]X$ (X = OTf, NTf_2).[13b] In all cases **4a**/AgOTf is markedly more efficient than its triphenylphosphine counterpart, which suggests that this analogy may have limited validity. The disparate performance of these system is clearly evident for the phenyl-substituted propargyl amide **7c**, which reached 74% conversion after only 30 min with 2 mol % **4a**/AgOTf, whereas $[Au(PPh_3)]NTf_2$ required 36 h to reach a comparable conversion, albeit with a slightly lower catalyst loading (1 mol %). Similarly, the cinnamyl substrate **7f** reached good conversion after 1.5 h using catalyst based on **3a**, whereas $[Au(PPh_3)]NTf_2$ required 36 h. At this stage we can only speculate about the origin of the disparate performance of these two systems but note that the non-phosphine-containing aryl ring in **3a** forms a weak interaction with gold, which is not possible for triphenylphosphine. The importance of the biaryl unit in facilitating palladium-catalyzed cross-coupling is well documented and has been shown to be associated at least in part with the formation of a weak stabilizing interaction between palladium and the non-phosphine-containing aryl ring. A corollary of this might be that a biaryl/biaryl-like unit is necessary for efficient catalysis regardless of the basicity of the phosphine, which may have only a minor influence on performance; in this regard a systematic comparison between **3a**, triphenylphosphine, PCy_2(*o*-biphenyl), PCy_3, and Ph_2P(*o*-biphenyl) might prove insightful.

Conclusions

In conclusion, electrophilic gold(I) complexes of KITPHOS monophosphines catalyze the 5-exo-dig cycloisomerization of a range of propargyl amides. Comparative catalyst testing has revealed that systems based on diphenylphosphino-substituted KITPHOS monophosphines outperform their electron-rich dicyclohexylphosphino-based counterparts and that the former are markedly more efficient than $[Au(PPh_3)]^+$, the benchmark complex previously used to catalyze this reaction. The first air-stable cationic gold(I) complex coordinated by an electron-rich monophosphine and tetrahydrothiophene to be isolated is a highly efficient cycloisomerization catalyst, giving conversions that match those obtained with the corresponding catalyst generated by chloride abstraction. Further studies are currently underway to (i) extend these cyclizations to the synthesis of a broader range of heterocycles, (ii) develop gold(I)-catalyzed cascade carbocyclizations for the construction of complex heteropolycyclic architectures, and (iii) further elaborate the products of cycloisomerization by incorporating them into novel tandem/sequential reaction sequences. Moreover, on the basis that new bulky triaryl-type monophosphines have recently been reported to outperform their triphenylphosphine counterparts in the hydrosilylation of bulky ketones[28] as well as the selective telomerization of 1,3-butadiene,[29] we anticipate that triaryl-like monophosphines based on the KITPHOS architecture may well find use in a wide range of platinum group metal-catalyzed transformations.

Experimental Section

General Comments. All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen or argon in oven-dried glassware. Dichloromethane and chloroform were distilled from calcium hydride, THF was distilled from sodium, and hexane and diethyl ether were distilled from Na/K alloy, under an atmosphere of nitrogen. All amines were purchased from commercial suppliers and purified by passing through a short column of alumina immediately prior to use. Phenylacetylene, 2-ethynylanisole, chlorodiphenylphosphine, and anthracene were purchased from commercial suppliers and used without further purification. (Diphenylphosphinoylethynyl)benzene (**1a**),[30] 11-(dicyclohexylphosphino)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene (**2c**),[8] 11-(dicyclohexylphosphino)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene (**2d**),[8] AuCl(tht),[14] and the propargyl amides[11] were prepared as previously described. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on JEOL LAMBDA-500 or ECS-400 instruments. Thin-layer chromatography was carried out on aluminum sheets precoated with silica gel 60F 254, and column chromatography was performed using Merck Kieselgel 60. Gas chromatography−mass spectrometry was performed on a Saturn 2220 GC-MS system using a factorFour VF-5 ms capillary column, 30 m, 0.25 mm, and 0.25 μm.

Synthesis of 2-(Diphenylphosphinoylethynyl)anisole (1b). To a solution of 2-ethynylanisole (2.50 g, 18.9 mmol) in THF (65 mL) cooled to −78 °C was added BuLi (7.56 mL, 2.5 M, 18.9 mmol). The reaction was allowed to warm to 0 °C, stirred for 30 min, and then cooled to −78 °C. Chlorodiphenylphosphine (3.40 mL, 18.4 mmol) was added dropwise, and the solution was allowed to warm to room temperature and stirred for a further 2.5 h. The reaction was then cooled to 0 °C and hydrogen peroxide (35% aqueous solution, 8.32 mL, 24.6 mmol) added. The solution was allowed to warm to room temperature and stirred for 30 min. Water (90 mL) was added and the product extracted with diethyl ether (3 × 40 mL). The organic fractions were combined and dried over $MgSO_4$, and the solvent was removed *in vacuo* to leave a yellow solid. Purification by column chromatography eluting with CH_2Cl_2/ethylacetate (2:3) gave the desired product as a white crystalline solid in 84% yield (5.2 g). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): 9.0. ^1H NMR (399.78 MHz, $CDCl_3$, δ): 7.33 (ddd, J = 14.2, 8.7, 1.8 Hz, 4H, Ar-*H*), 7.44−7.39 (m, 7H, Ar-*H*), 7.32 (td, J = 8.7, 1.9 Hz, 1H, Ar-*H*), 6.85 (t, J = 7.7 Hz, 1H, Ar-*H*), 6.83 (d, J = 6.4 Hz, 1H, Ar-*H*), 3.82 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 161.7 (C_6H_4), 134.1 (C_6H_5), 133.5 (d, J = 121 Hz, C_6H_4), 132.3 (C_6H_4), 132.0 (d, J = 2.9 Hz, C_6H_5), 131.0 (d, J = 11.5 Hz, C_6H_5), 128.7 (d, J = 13.4 Hz, C_6H_5), 120.6 (C_6H_4), 110.7 (C_6H_4), 109.2 (d, J = 3.1 Hz, C_6H_4), 102.8 (d, J = 30.5 Hz, $C{\equiv}CP$), 85.6 (d, J = 172.6 Hz,

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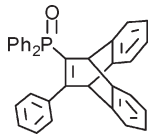
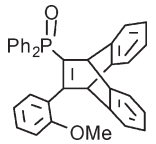
(30) Liu, B.; Wang, K. K.; Petersen, J. L. *J. Org. Chem.* **1996**, *61*, 8503.

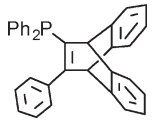
C≡*C*P), 55.7 (O*C*H$_3$). LRMS (EI$^+$): *m*/*z* 333 [M + H]$^+$. HRMS (ESI$^+$): exact mass calcd for $C_{21}H_{18}O_2P$ [M + H]$^+$ requires *m*/*z* 333.1044, found *m*/*z* 333.1043. Anal. Calcd for $C_{21}H_{17}O_2P$: C, 75.90; H, 5.16. Found: C, 76.32; H, 5.44.



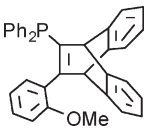
Synthesis of 2-(Diphenylphosphinoyl)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene (2a). (Diphenylphosphinoylethynyl)benzene (2.0 g, 6.58 mmol) and anthracene (4.72 g, 26.5 mmol) were mixed in a flask, which was gradually heated to 220 °C using a DrySyn multiposition heating block. The temperature was then lowered to 200 °C and the mixture heated for a further 10 h. The resulting dark solid residue was purified by column chromatography eluting with CH_2Cl_2/ethyl acetate (2:3) to afford **2a** as an off-white solid in 81% yield (2.55 g). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): 25.5. ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.43 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.41 (d, *J* = 7.8 Hz, 2H, Ar-*H*), 7.36 (m, 4H, Ar-*H*), 7.25 (t br, *J* = 9.5 Hz, 4H, Ar-*H*), 7.11 (t br, *J* = 6.3 Hz, 4H, Ar-*H*), 7.06−6.98 (m, 7H, Ar-*H*), 5.42 (d, *J* = 2.8 Hz, 1H, bridgehead C*H*), 5.26 (d, *J* = 8.7 Hz, 1H, bridgehead C*H*). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 166.2 (d, *J* = 7.6 Hz, *C*═CP), 144.5 (C_6H_4Q), 144.3 (C_6H_4Q), 137.6 (d, *J* = 4.8 Hz, C_6H_5Q), 136.5 (d, *J* = 101 Hz, C═*C*P), 132.9 (d, *J* = 105 Hz, C_6H_5Q), 131.7 (C_6H_5), 131.6 (C_6H_5), 131.4 (C_6H_5), 128.3 (d, *J* = 12.4 Hz, C_6H_5), 128.1 (C_6H_5), 127.7 (C_6H_5), 125.3 (C_6H_4), 125.1 (C_6H_4), 123.7 (C_6H_4), 123.4 (C_6H_4), 61.0 (d, *J* = 9.5 Hz, bridgehead *C*H), 53.7 (d, *J* = 10.4 Hz, bridgehead *C*H). LRMS (EI$^+$): *m*/*z* 481 [M + H]$^+$. HRMS (ESI$^+$): exact mass calcd for $C_{34}H_{26}OP$ [M + H]$^+$ requires *m*/*z* 481.1721, found *m*/*z* 481.1724. Anal. Calcd for $C_{34}H_{25}OP$: C, 84.98; H, 5.24. Found: C, 85.31; H, 5.62.



Synthesis of 11-(Diphenylphosphinoyl)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene (2b). Compound **2b** was prepared from 2-(diphenylphosphinoylethynyl)anisole (2.0 g, 6.01 mmol) according to the procedure described above for **2a** and isolated as an analytically pure off-white solid in 77% yield (2.36 g) after purification by column chromatography eluting with CH_2Cl_2/ethyl acetate (1:1). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): 25.8. ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.5−6.87 (br m, 19H, Ar-*H*), 6.69 (dd, *J* = 7.4, 1.9 Hz, 1H, Ar-*H*), 6.43 (d, *J* = 8.2 Hz, 1H, Ar-*H*), 6.39 (t, *J* = 7.6 Hz, Ar-*H*), 5.20 (d, *J* = 4.1 Hz, 1H, bridgehead C*H*), 5.18 (d, *J* = 9.7 Hz, 1H, bridgehead C*H*), 3.57 (s, 3H, OC*H*$_3$). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 165.6 (d, *J* = 11.4 Hz, *C*═CP), 156.2, 145.3 (br), 144.4 (br), 137.0 (d, *J* = 103 Hz), 133.2 (br), 132.2 (br), 131.5 (br), 130.7, 129.7, 128.0 (br), 126.6, 124.9 (br), 124.8, 123.6, 119.9, 109.7, 60.1 (d, *J* = 7.6 Hz, bridgehead *C*H), 54.7 (OCH$_3$), 53.6 (d, *J* = 7.4 Hz, bridgehead *C*H). LRMS (EI$^+$) *m*/*z* 511 [M + H]$^+$. HRMS (ESI$^+$): exact mass calcd for $C_{35}H_{28}O_2P$ [M + H]$^+$ requires *m*/*z* 511.1827, found *m*/*z* 511.1816. Anal. Calcd for $C_{35}H_{27}O_2P$: C, 82.34; H, 5.33. Found: C, 82.66; H, 5.41.



Reduction of 2a to 11-(Diphenylphosphino)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene (3a). A flame-dried Schlenk flask was charged with **2a** (4.0 g, 8.33 mmol), toluene (70 mL), and triethylamine (40 mL, 287 mmol). Trichlorosilane (8.35 mL, 82.6 mmol) was added slowly and the mixture heated at 110 °C for 2 days. The reaction mixture was diluted with diethyl ether (100 mL) and added slowly to a mixture of ice (60 g) and 20% aqueous NaOH (110 mL). After stirring vigorously at room temperature for 30 min, the organic layer was removed and the aqueous phase extracted with diethyl ether (3 × 100 mL). The organic fractions were combined, washed with saturated $NaHCO_3$ (2 × 100 mL), water (2 × 100 mL), and brine (2 × 100 mL), dried over $MgSO_4$, and filtered, and the solvent was removed *in vacuo*. The product was purified by column chromatography eluting with hexane/ethyl acetate (9:1) to afford **3a** as a spectroscopically pure white solid in 67% yield (2.59 g). An analytically pure sample was obtained by slow diffusion of a chloroform solution layered with hexane at room temperature. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): −12.8. ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.38−7.31 (m, 13H, Ar-*H*), 7.22 (br t, *J* = 6.9 Hz, 4H, Ar-*H*), 6.98 (t, *J* = 6.9 Hz, 2H, Ar-*H*), 6.91 (t, *J* = 6.9 Hz, 2H, Ar-*H*), 6.81 (d, *J* = 7.3 Hz, 2H, Ar-*H*), 5.54 (d, *J* = 2.6 Hz, 1H, bridgehead C*H*), 5.06 (d, *J* = 1.5 Hz, 1H, bridgehead C*H*). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 163.6 (d, *J* = 22.9 Hz, *C*═CP), 145.8 (C_6H_4Q), 145.2 (C_6H_4Q), 139.3 (d, *J* = 22.9 Hz, C═*C*P), 138.7 (d, *J* = 5.7 Hz, C_6H_5Q), 137.0 (d, *J* = 11.4 Hz, C_6H_5Q), 133.4 (C_6H_5), 133.2 (C_6H_5), 128.5 (d, *J* = 5.7 Hz, C_6H_5), 128.4 (C_6H_5), 128.2 (C_6H_5), 128.1 (C_6H_5), 124.7 (C_6H_4), 124.6 (C_6H_4), 123.3 (C_6H_4), 122.8 (C_6H_4), 59.4 (d, *J* = 6.7 Hz, bridgehead *C*H), 55.2 (d, *J* = 5.7 Hz, bridgehead *C*H). LRMS (EI$^+$) *m*/*z* 465 [M + H]$^+$. HRMS (ESI$^+$): exact mass calcd for $C_{34}H_{26}P$ [M + H]$^+$ requires *m*/*z* 465.1722, found *m*/*z* 465.1772. Anal. Calcd for $C_{34}H_{25}P$: C, 87.91; H, 5.42. Found: C, 88.24; H, 5.55.



Reduction of 2b to 11-(Diphenylphosphino)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene (3b). Compound **2b** (3.5 g, 6.86 mmol) was reduced according to the procedure described above for **2a** to afford **3b** as an off-white solid in 66% yield (2.24 g) after purification by column chromatography, eluting with hexane/ethyl acetate (85:15). An analytically and spectroscopically pure sample was obtained by slow diffusion of a chloroform solution layered with hexane at room temperature. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): −13.9. ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.35−7.19 (br m, 12H, Ar-*H*), 6.97 (t, *J* = 7.3 Hz, 2H, Ar-*H*), 6.92 (d, *J* = 8.3 Hz, 1H, Ar-*H*), 6.90 (br t, *J* = 7.3 Hz, 2H, Ar-*H*), 6.83 (t, *J* = 7.4 Hz, 1H, Ar-*H*), 6.80 (br, 4H, Ar-*H*), 5.46 (d, *J* = 2.8 Hz, 1H, bridgehead C*H*), 5.02 (d, *J* = 1.8 Hz, 1H, bridgehead C*H*), 3.72 (s, 3H, OC*H*$_3$). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 163.2 (d, *J* = 30.5 Hz, *C*═CP), 157.4 (C_6H_4OMe), 146.1 (br, C_6H_5), 145.7 (2 × C_6H_4), 139.9 (d, *J* = 21.1 Hz, C_6H_4OMe), 137.3 (d, *J* = 11.4 Hz, C_6H_4OMe), 133.4 (C_6H_5), 133.2 (C_6H_5), 130.8 (d, *J* = 6.7 Hz, C_6H_5), 129.7 (C_6H_5), 128.4 (d, *J* = 5.8 Hz, C_6H_5), 128.2 (C_6H_5), 128.0 (d, *J* = 6.7 Hz, C_6H_4OMe), 124.4 (C_6H_4), 124.3 (C_6H_4), 123.5 (C_6H_4), 123.1 (C_6H_4), 120.0 (C_6H_4OMe), 111.0 (C_6H_4OMe), 58.8 (d, *J* = 6.7 Hz, bridgehead *C*H), 55.3 (OCH$_3$), 54.9 (d, *J* = 5.7 Hz, bridgehead *C*H). LRMS (EI$^+$): *m*/*z* 495 [M + H]$^+$. HRMS (ESI$^+$) exact mass calcd for $C_{35}H_{28}OP$ [M + H]$^+$ requires *m*/*z* 495.1878, found *m*/*z* 495.1858. Anal. Calcd for $C_{35}H_{27}OP$: C, 85.00; H, 5.50. Found: C, 85.35; H, 5.73.

Synthesis of [{2-(Diphenylphosphino)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene}AuCl] (4a). To a solution of Au(tht)Cl (0.25 g, 0.78 mmol) in dichloromethane (8−10 mL) was added a solution of **3a** (0.37 g, 0.80 mmol) in dichloromethane (2−3 mL). After stirring for 1 h the solvent was removed under reduced pressure and the resulting white solid triturated with diethyl

ether (2 × 5 mL). Crystallization by slow diffusion of a chloroform solution layered with hexane at room temperature gave **4a** in 79% yield (0.43 g). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): 23.2. ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.54 (t, J = 7.4 Hz, 2H Ar-*H*), 7.46−7.30 (m, 13H, Ar-*H*), 7.07 (m, 4H, Ar-*H*), 6.99 (t, J = 7.4 Hz, 2H, Ar-*H*), 6.87 (t, J = 6.9 Hz, 2H, Ar-*H*), 5.50 (d, J = 4.3 Hz, 1H, bridgehead C*H*), 4.98 (d, J = 7.8 Hz, 1H, bridgehead C*H*). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 169.1 (d, J = 30.5 Hz, *C*=CP), 144.3 (C_6H_4Q), 144.2 (C_6H_4Q), 137.3 (d, J = 6.7 Hz, C_6H_5Q), 133.9 (d, J = 14.3 Hz, C_6H_5), 132.1 (d, J = 57.2 Hz, C=*C*P), 131.8 (C_6H_5), 129.7 (C_6H_5), 129.4 (C_6H_5), 129.2 (C_6H_5), 129.1 (C_6H_5), 128.8 (C_6H_5), 125.6 (C_6H_4), 125.3 (C_6H_4), 123.6 (C_6H_4), 123.3 (C_6H_4), 60.8 (d, J = 8.6 Hz, bridgehead *C*H), 54.8 (d, J = 4.7 Hz, bridgehead *C*H). Anal. Calcd for $C_{34}H_{25}AuClP$: C, 58.59; H, 3.62. Found: C, 58.81; H, 3.97.

Synthesis of [{11-(Diphenylphosphino)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene}AuCl] (4b). Compound **4b** was prepared according to the procedure described above for **4a** on the same scale and isolated as a white solid in 63% yield (0.36 g) by slow diffusion of hexane into a chloroform solution at room temperature. $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): 23.7. ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.51 (m br, 2H Ar-H), 7.45−7.34 (m, 8H, Ar-*H*), 7.35 (d br, J = 11.7 Hz, 1H, Ar-*H*), 7.28 (d br, J = 7.3 Hz, 2H, Ar-*H*), 7.06−6.99 (m br, 4H, Ar-*H*), 6.95 (br d, J = 7.3 Hz, 1H, Ar-*H*), 6.91 (d, J = 7.8 Hz, 1H, Ar-*H*), 6.79 (td, J = 7.3, 0.9 Hz, 1H, Ar-*H*), 6.70 (br d, J = 11.7 Hz, 1H, Ar-*H*), 6.66 (dd, J = 7.4, 1.4 Hz, 1H, Ar-*H*), 5.44 (d, J = 4.1 Hz, 1H, bridgehead C*H*), 4.95 (d, J = 7.8 Hz, 1H, bridgehead C*H*), 3.63 (s, 3H, OC*H*$_3$). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 167.8 (d, J = 13.4 Hz, *C*=CP), 156.8 (C_6H_4OMe), 144.9 (C_6H_5Q), 144.7 (C_6H_4Q), 143.9 (C_6H_4Q), 133.9 (C_6H_5), 133.8 (C_6H_5), 132.5 (d, J = 60.1 Hz, C=*C*P), 131.5 (br d, J = 37.2 Hz, C_6H_5), 131.1 (C_6H_4OMe), 129.9 (C_6H_4OMe), 129.2 (br d, J = 12.4 Hz, C_6H_5), 128.9 (br d, J = 11.4 Hz, C_6H_5), 126.3 (d, J = 7.6 Hz, C_6H_4OMe), 125.2 (br d, J = 28.6 Hz, C_6H_4), 124.9 (br d, J = 33.3 Hz, C_6H_4), 123.7 (C_6H_4), 123.0 (br d, J = 2.4 Hz, C_6H_4), 120.5 (C_6H_4OMe), 111.5 (C_6H_4OMe), 60.1 (d, J = 8.5 Hz, bridgehead *C*H), 54.0 (OCH_3), 54.6 (d, J = 5.7 Hz, bridgehead *C*H). Anal. Calcd for $C_{35}H_{27}AuClOP$: C, 57.82; H, 3.74. Found: C, 58.12; H, 4.03.

Synthesis of [{2-(Dicyclohexylphosphino)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene}AuCl] (4c). Compound **4c** was prepared according to the procedure described above for **4a** on the same scale and isolated as a white solid in 92% yield (0.507 g) after trituration with diethyl ether (2 × 5 mL). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): 37.1. ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.40 (t, J = 6.4 Hz, 1H, Ar-*H*), 7.33 (td, J = 7.8, 1.4 Hz, 2H, Ar-*H*), 7.30−7.24 (m, 4H, Ar-*H*), 7.01−6.96 (m, 4H, Ar-*H*), 6.84 (dd, J = 6.9, 1.4 Hz, 2H, Ar-*H*), 5.32 (d, J = 5.5 Hz, 1H, bridgehead C*H*), 5.17 (d, J = 3.6 Hz, 1H, bridgehead C*H*), 2.12 (br m, 2H, Cy-*H*), 1.86 (br, 2H, Cy-*H*), 1.73 (br, 2H, Cy-*H*), 1.56 (br m, 6H, Cy-*H*), 1.30−1.02 (m, 10H, Cy-*H*); $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 167.8 (d, J = 14.3 Hz, *C*=CP), 144.2 (C_6H_4Q), 143.8 (C_6H_4Q), 139.0 (d, J = 6.7 Hz, C_6H_5Q), 132.5 (d, J = 49.6 Hz, C=*C*P), 129.3 (C_6H_5), 128.8 (C_6H_5), 126.9 (C_6H_5), 125.6 (C_6H_4), 125.3 (C_6H_4), 123.6 (C_6H_4), 123.0 (C_6H_4), 61.2 (d, J = 7.6 Hz, bridgehead C*H*), 54.6 (d, J = 4.6 Hz, bridgehead C*H*); 35.2 (d, J = 35.3 Hz, Cy), 30.4 (d, J = 4.7 Hz, Cy), 29.8 (Cy), 26.6 (d, J = 7.6 Hz, Cy), 26.4 (d, J = 5.7 Hz, Cy), 25.6 (Cy). Anal. Calcd for $C_{34}H_{37}AuClP$: C, 57.59; H, 5.26. Found: C, 57.71; H, 5.32.

Synthesis of [{11-(Dicyclohexylphosphino)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene}AuCl] (4d). Compound **4d** was prepared according to the procedure described above for **4a** on the same scale and isolated as a white solid in 84% yield (0.48 g) by slow diffusion of hexane into a chloroform solution at room temperature. $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, δ): 37.5. ^1H NMR (399.78 MHz, $CDCl_3$, δ): 7.44 (td, J = 7.8, 1.8 Hz, 1H, Ar-*H*), 7.32 (d, J = 8.2 Hz, 1H, Ar-*H*), 7.30 (t, J = 7.8 Hz, 2H, Ar-*H*), 7.22 (dd, J = 9.6, 1.9 Hz, 1H, Ar-*H*), 7.02−6.99 (m, 4H, Ar-*H*), 6.94 (d, J = 8.7 Hz, 2H, Ar-*H*), 6.67 (dd, J = 7.3, 1.4 Hz, 1H, Ar-*H*), 5.34 (d, J = 5.5 Hz, 1H, bridgehead C*H*), 5.16 (d, J = 3.2 Hz, 1H, bridgehead C*H*), 2.16 (br m, 2H, Cy-*H*), 1.93−1.50 (m, 8H, Cy-*H*), 1.34−1.05 (m, 12H, Cy-*H*). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 168.3 (d, J = 11.4 Hz, *C*=CP), 156.7 (C_6H_4OMe), 144.9 (C_6H_4Q), 144.9 (C_6H_4Q), 144.1 (C_6H_4Q), 143.5 (C_6H_4Q), 132.6 (d, J = 49.6 Hz, C=*C*P), 130.4 (C_6H_4OMe), 129.3 (C_6H_4OMe), 127.7 (d, J = 6.7 Hz, C_6H_4OMe), 125.4 (C_6H_4), 125.2 (C_6H_4), 125.1 (C_6H_4), 124.7 (C_6H_4), 123.8 (C_6H_4), 123.7 (C_6H_4), 122.8 (C_6H_4), 122.6 (C_6H_4), 121.0 (C_6H_4OMe), 111.2 (C_6H_4OMe), 60.3 (d, J = 7.6 Hz, bridgehead *C*H), 54.9 (OCH_3), 54.6 (d, J = 4.2 Hz, bridgehead *C*H), 35.5 (d, J = 35.1 Hz, Cy), 35.2 (d, J = 35.3 Hz, Cy), 31.1 (d, J = 3.8 Hz, Cy), 29.9 (Cy), 29.7 (d, J = 2.9 Hz, Cy), 29.7 (Cy), 26.9 (d, J = 12.4 Hz, Cy), 26.7 (Cy), 26.6 (Cy), 26.4 (d, J = 13.3 Hz, Cy), 25.8 (Cy), 25.6 (Cy). Anal. Calcd for $C_{35}H_{39}AuClOP$: C, 56.88; H, 5.32. Found: C, 57.09; H, 5.44.

Synthesis of [{11-(Dicyclohexylphosphino)-12-(2-methoxyphenyl)-9,10-dihydro-9,10-ethenoanthracene}Au(SO_3CF_3)] (5). A flame-dried Schlenk flask charged with **4d** (0.30 g, 4.06 mmol), AgOTf (0.104 g, 4.06 mmol), and CH_2Cl_2 (10 mL) was stirred at room temperature for 60 min, after which time the cloudy solution was filtered, the solvent removed *in vacuo*, and the residue crystallized by slow diffusion of hexane into a dichloromethane solution to give **5** as colorless crystals in 64% yield (0.22 g). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$, δ): 34.3. ^1H NMR (399.78 MHz, $CDCl_3$, δ): 7.45 (td, J = 8.8, 1.9 Hz, 1H, Ar-*H*), 7.34 (td, J = 8.3, 1.4 Hz, 2H, Ar-*H*), 7.31 (d, J = 7.8 Hz, 1H, Ar-*H*), 7.25 (d, J = 7.8 Hz, 1H), 7.08−7.03 (m, 4H, Ar-*H*), 6.97 (t, J = 8.2 Hz, 2H, Ar-*H*), 6.67 (dd, J = 7.4, 1.9 Hz, 1H, Ar-*H*), 5.35 (d, J = 5.5 Hz, 1H, bridgehead C*H*), 5.20 (d, J = 3.7 Hz, 1H, bridgehead C*H*), 3.61 (s, 3H, OCH_3), 2.18−1.53 (m, 12H, Cy-*H*), 1.36−1.04 (m, 10H, Cy-*H*). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 169.8 (d, J = 10.5 Hz, *C*=CP), 156.6 (C_6H_4OMe), 144.6 (C_6H_4Q), 144.5 (C_6H_4Q), 143.8 (C_6H_4Q), 143.2 (C_6H_4Q), 130.9 (C_6H_4OMe), 132.6 (d, J = 56.2 Hz, C=*C*P), 128.9 (C_6H_4OMe), 127.2 (d, J = 7.6 Hz, C_6H_4OMe), 125.6 (C_6H_4), 125.4 (C_6H_4), 125.3 (C_6H_4), 124.9 (C_6H_4), 123.9 (C_6H_4), 123.9 (C_6H_4), 122.7 (C_6H_4), 122.5 (C_6H_4), 120.7 (C_6H_4OMe), 120.1 (q, J = 316 Hz, CF_3SO_3), 111.5 (C_6H_4OMe), 60.2 (d, J = 7.6 Hz, bridgehead *C*H), 54.9 (OCH_3), 54.1 (d, J = 3.82 Hz, bridgehead *C*H), 35.1 (d, J = 37.1 Hz, Cy), 34.8 (d, J = 36.2 Hz, Cy), 31.2 (d, J = 3.9 Hz, Cy), 29.9 (2 × Cy), 29.6 (Cy), 26.9 (d, J = 12.3 Hz, Cy), 26.5 (d, J = 3.8 Hz, Cy), 26.4 (d, J = 2.8 Hz, Cy), 26.3 (d, J = 13.3 Hz, Cy), 25.7 (Cy), 25.5 (Cy). Anal. Calcd for $C_{36}H_{39}AuF_3O_4PS$: C, 50.71; H, 4.61. Found: C, 51.03; H, 4.78.

Synthesis of [{2-(Dicyclohexylphosphino)-12-phenyl-9,10-dihydro-9,10-ethenoanthracene}Au(tht)][SO_3CF_3] (6). To a solution of Au(tht)Cl (0.200 g, 0.63 mmol) and tetrahydrothiophene (0.11 mL, 1.26 mmol) in dichloromethane (10 mL) was added a solution of **3c** (0.302 g, 0.65 mmol) in dichloromethane (2−3 mL), and the resulting mixture was stirred for 1 h, after which time silver trifluoromethanesulfonate (0.16 g, 0.63 mmol) was added. The reaction mixture was stirred for an additional 30 min and filtered, and the solvent was removed under reduced pressure to afford **6** as a white powder. Crystallization by slow diffusion of a chloroform solution layered with hexane at room temperature gave **6** in 71% yield (0.406 g). $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$, δ): 40.6. ^1H NMR (500.16 MHz, $CDCl_3$, δ): 7.45 (m, 5H, Ar-*H*), 7.30 (dd, J = 5.9, 1.9 Hz, 2H, Ar-*H*), 7.04 (m, 4H, Ar-*H*), 6.96 (dd, J = 5.9, 1.9 Hz, 2H, Ar-*H*), 5.58 (d, J = 5.1 Hz, 1H, bridgehead C*H*), 5.22 (d, J = 7.1 Hz, 1H, bridgehead C*H*), 3.0 (br t, J = 6.4 Hz, 4H, SCH_2), 2.55 (br q, J = 9.4 Hz, 2H, Cy-*H*), 1.99 (m, 6H, SCH_2CH_2 + Cy-*H*), 1.82 (br d, J = 11.4 Hz, 2H, Cy-*H*), 1.69 (br t, J = 11.4 Hz, 4H, Cy-*H*), 1.47 (br q, J = 12.8 Hz, 2H, Cy-*H*), 1.34 (br, 2H, Cy-*H*), 1.25 (br q, J = 12.8 Hz, 2H, Cy-*H*), 1.09 (m, 6H, Cy-*H*). $^{13}C\{^1H\}$ NMR (125.76 MHz, $CDCl_3$, δ): 170.4 (d, J = 11.4 Hz, *C*=CP), 143.9 (C_6H_4Q), 143.1 (C_6H_4Q), 139.8 (d, J = 6.7 Hz, C_6H_5Q), 133.2 (d, J =

Table 2. Crystallographic Data

	4b	**4d**	**5**	**6**
chem form	$C_{35}H_{27}AuClOP\cdot CH_2Cl_2$	$C_{35}H_{39}AuClOP\cdot 0.5CH_2Cl_2$	$C_{36}H_{39}AuF_3O_4PS$	$C_{38}H_{45}AuPS^+\cdot CF_3O_3S^-\cdot CHCl_3$
form wt	811.9	781.5	852.7	1030.2
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	13.5161(3)	11.7404(3)	20.9477(4)	9.0277(6)
b (Å)	17.2666(4)	20.3209(4)	19.3370(3)	19.2721(11)
c (Å)	15.3084(4)	13.8375(3)	16.9133(2)	24.1482(14)
β (deg)	112.921(3)	103.601(2)	96.282(1)	98.851(6)
V (Å^3)	3290.54(14)	3208.71(12)	6809.86(19)	4151.3(4)
Z	4	4	8	4
μ (mm^{-1})	4.791	4.828	4.483	3.926
reflns measd	22 102	19 318	51 986	34 976
unique reflns	7151	6721	11 965	7295
R_{int}	0.0347	0.0331	0.0525	0.0735
refined params	353	353	831	478
R (F, $F^2 > 2\sigma$)	0.0304	0.0226	0.0295	0.0505
R_w (F^2, all data)	0.0690	0.0451	0.0557	0.1311
GoF (F^2)	0.920	0.929	0.850	1.010
diff map extremes (e Å^{-3})	2.82, −1.36	0.87, −0.91	1.94, −2.07	1.71, −2.47

47.6 Hz, C═*C*P), 129.6 (C_6H_5), 128.8 (C_6H_5), 127.3 (C_6H_5), 125.8 (C_6H_4), 125.6 (C_6H_4), 123.6 (C_6H_4), 123.5 (C_6H_4), 121.2 (q, J = 318.6 Hz, CF_3SO_3), 61.0 (d, J = 7.6 Hz, bridgehead *C*H), 54.1 (bridgehead *C*H), 39.0 (SCH_2), 34.4 (d, J = 34.3 Hz, Cy), 30.9 (SCH_2CH_2 + Cy), 30.5 (Cy), 26.4 (Cy), 26.2 (Cy), 25.3 (Cy). Anal. Calcd for $C_{39}H_{45}AuF_3O_3PS_2$: C, 51.43; H, 4.98. Found: C, 51.67; H, 5.05.

General Procedure for the Gold-Catalyzed Cycloisomerizations Using Precursors 4a−d. A flame-dried Schlenk flask charged with **4a−d** (0.01 mmol), AgOTf (0.0026 g, 0.01 mmol), and dichloromethane (1.0 mL) was stirred for 30 min, after which propargyl amide (0.5 mmol) was added and the resulting mixture stirred for the allocated time. The reaction mixture was diluted with diethyl ether, 1,3-dinitrobenzene was added (0.084 g, 0.5 mmol), and the resulting mixture was passed through a short silica plug. The solvent was removed and the residue analyzed by ^{1}H NMR spectroscopy to determine conversions before being purified by column chromatography, eluting with hexane/ethyl acetate. Known products were characterized by NMR spectroscopy and mass spectrometry and unknown products by NMR spectroscopy, mass spectrometry, and high-resolution mass spectrometry.

General Procedure for the Gold-Catalyzed Cycloisomerizations Using 5 and 6. A flame-dried Schlenk flask was charged with **5** or **6** (0.01 mmol), propargyl amide (0.5 mmol), and dichloromethane (1.0 mL), and the resulting mixture was stirred for the allocated time. The reaction mixture was diluted with diethyl ether, 1,3-dinitrobenzene was added (0.084 g, 0.5 mmol), and the resulting mixture was passed through a short silica plug. The solvent was removed and the residue analyzed by ^{1}H NMR spectroscopy to determine conversions before being purified by column chromatography, eluting with hexane/ethyl acetate. Known products were characterized by NMR spectroscopy and mass spectrometry and unknown products by NMR spectroscopy, mass spectrometry, and high-resolution mass spectrometry (HRMS).

X-ray Crystallography. All data were measured on an Oxford Diffraction Gemini A Ultra diffractometer at 150 K, with Mo Kα radiation (λ = 0.71073 Å). Semiempirical absorption corrections were applied, based on symmetry-equivalent and repeated reflections. Structures were solved by direct methods and refined on all unique F^2 values, with anisotropic non-H atoms and constrained riding isotropic H atoms. Disordered dichloromethane solvent molecules could not be modeled as discrete atoms for **4b** and **4d** and were treated by the SQUEEZE procedure of PLATON.[31] High anisotropy of some atoms of **6** indicated possible disorder, but this could not be resolved and has been ignored. Programs were CrysAlisPro for data collection, integration, and absorption corrections[32] and SHELXTL for structure solution, refinement, and graphics.[33] A summary of key crystallographic experimental information is provided in Table 2, and full details are in the Supporting Information.

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Note Added after ASAP Publication: This paper was published on the Web on Aug 17, 2010, with errors in the fifth paragraph of the Results and Discussion section and in Equation 1. The corrected version was reposted on Aug 23, 2010.

Supporting Information Available: Full details of experimental procedures, characterization data for all new compounds, details of catalyst testing, and, for compounds **4b**, **4d**, **5**, and **6**, full details of crystal data, structure solution and refinement, atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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