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Tertiary Amino Group in Cationic Gold Catalyst: Tethered Frustrated Lewis Pairs That Enable Ligand-Controlled Regiodivergent and Stereoselective Isomerizations of Propargylic Esters

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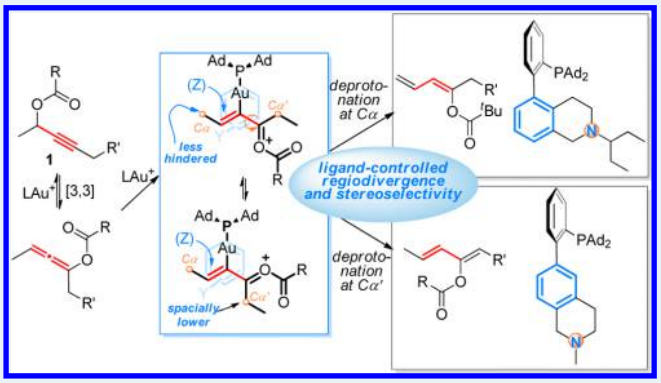
Supporting Information

ABSTRACT: The development of novel ligands specifically tailored for homogeneous gold catalysis is essential for a new generation of gold catalysis. In this work, we report the development of remotely functionalized biphenyl-2-ylphosphine ligands based on strategic positioning in cationic gold catalysts of frustrated Lewis pairs (FLP), that is, basic tertiary amine moieties and the acidic gold center. By rationally tuning the location and size of the basic group, these Lewis pairs exhibit little or modest quenching and importantly enable regiodivergent and stereoselective isomerizations of propargylic esters into synthetically versatile dienyl esters under exceptionally mild conditions. Notably, the implementation of the concept of FLP in gold catalysis is rare.



KEYWORDS: *gold, catalysis, ligand, frustrated Lewis pair, regiodivergent, design, tertiary amine*

Homogeneous gold catalysis[1] has experienced exponential development since the beginning of the new millenium and is increasingly applied as enabling technologies/transformations in modern synthesis.[1d,2] In the process, ligands in the predominantly employed cationic gold(I) catalysts, that is, **L**Au$^+$ (**L**: ligand), have played an increasingly important role in enabling low catalyst loadings, novel reactivities, and achieving desirable selectivities. Despite their essential roles in catalysis, novel ones[3] designed to specifically take advantage of the linear structure of **L**-Au-(alkyne centroid) had been scarcely documented.

On the other hand, another area of exceptional advance that coincides with gold catalysis is the chemistry of frustrated Lewis pairs (FLP).[4] Despite that most FLPs are non-metal-based, recent developments have evolved to include metal as the Lewis acid component.[5] Considering that cationic Au(I) mostly behaves as a soft Lewis acid, it is surprising that these two rapidly growing areas have by far not overlapped.[6] With a few exceptions[7,8] that require excessive heating (≥110 °C),[7c,d] favorable intramolecular scenarios,[7b,e,f] or redox on Au,[7g] reactions catalyzed by cationic Au(I) are generally prohibited in the presence of basic aliphatic amine bases due to the formation of Lewis adduct. *It is, however, important to note that less-basic anilines are well-tolerated and not detrimental to gold catalysis*. We anticipate that the application of FLP in gold chemistry would facilitate the use of a stronger and generally inhibitive base in gold-catalyzed reactions and hence enrich both areas of research.

It is envisioned that via rational ligand design, tethered Lewis pairs consisting of an acidic cationic Au(I) and a basic tertiary amine could be made frustrated intramolecularly by spatial separation and intermolecularly by steric hindrance, as outlined in Scheme 1A. Our recent work[9] on rationally designed ligands offers a unique opportunity to apply the concept into practice. As shown in Scheme 1B, we developed novel biphenyl-2-ylphosphine ligands featuring functional groups at the 3′/4′-positions, at which has been reported few functional modifications[10] despite extensive study of this class of previledged ligands in catalysis.[11] The gold(I) complexes derived from these novel ligands, because of its linear P-Au-(alkyne centroid) structure and the restriction of rotation of the C2−P bond by bulky adamantyl groups, place the coordinated C−C triple bond or incoming nucleophiles right around the remote functional group and therefore enable their beneficial interactions. With an 3′-amide group, a ppm-level gold-catalyzed acid addition to alkyne is realized via dramatic reaction acceleration.[9a] With a weakly basic 3′-anilinic amine instead, as shown in Scheme 1C, the new ligand **L1** elicits unprecedented isomerization of certain alkynes into dienes.[9b] Mechanistically, the reaction is composed of two proton shuttlings, and the first one likely necessitates a propargylic C−H deprotonation by an aniline, thereby bridging a daunting pK_a difference of >26 units in DMSO and highlighting the potential of designing ligands specially tailored to linear Au(I) coordination structure. In the second proton shuttling, an 2-

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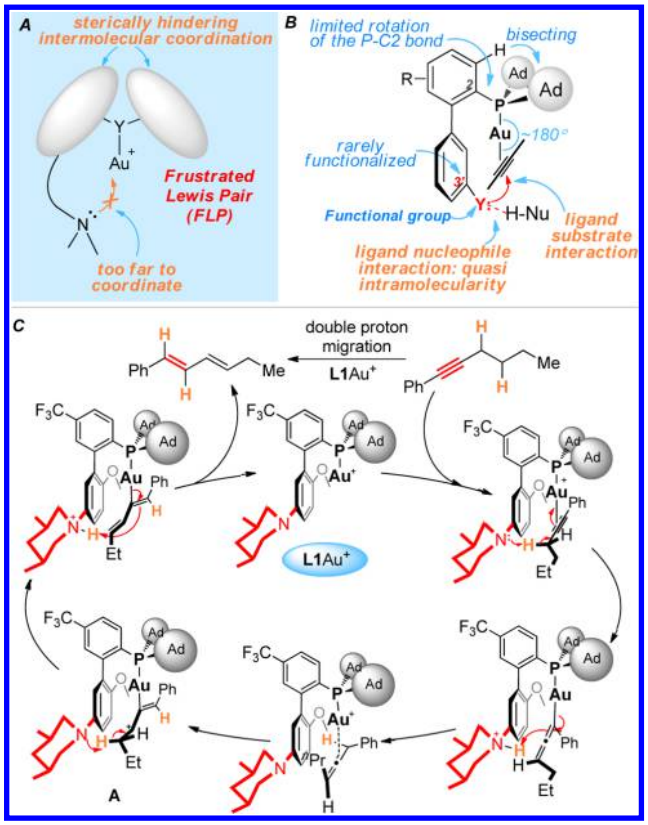
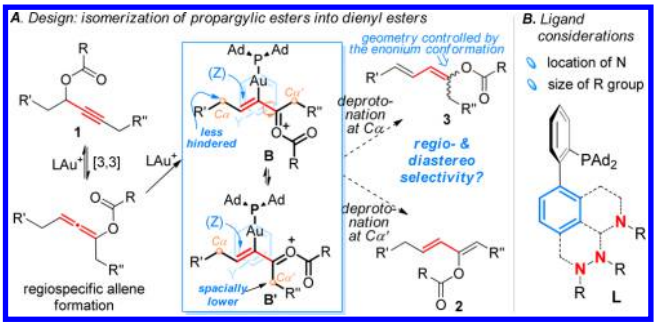
Scheme 1. (A) Conceptual Gold Complex Featuring FLP. (B) General Design of Remotely Functionalized Biphenyl-2-Ylphosphine Specifically Accommodating Au(I) Catalysis. (C) Designed Ligand-Enabled Isomerization of Alkynes into Dienes



auroallylic cation **A** is likely formed from the allene intermediate and subsequently deprotonated as a result of the promixity of the 3′-aniline group to its α-hydrogens. While **L1**Au$^+$ has the appearance of a FLP, anilines do not prohibit gold catalysis because of their weak basicity.

A major issue with the isomerization of alkynes into dienes is the lack of regiochemical controls when internal aliphatic alkynes are used as substrates. We anticipated that the regiochemical issues in the allene formation (i.e., the first proton shuttling in Scheme 1C) can be avoided by employing an alternative regiospecific generation instead of the alkyne isomerization, and the challenging regioselectivity pertaining to the isomerization of allene into diene can be addressed by optimally positioning the ligand remote basic moiety and tuning its size. To this end, as shown in Scheme 2A, the targeted chemistry would entail the access of regiodefined allenes in the form of carboxyallenes via our previously reported gold-catalyzed 3,3-rearrangement of propargylic esters.[12] Further activation of the in situ-generated carboxyallenes by the same gold catalyst will form an 1-acyloxy-2-auroallylic cation, as depicted in the two representative and relevant conformers **B** and **B′**, where the geometry of the alkenylgold should be predonimantly (Z).[13] For the two competing deprotonation sites, Cα and Cα', Cα can be sterically more accessible in both conformers, and Cα' in **B′** is spacially located lower than Cα. It is anticipated that these differences would be harnessed by strategic placing of a basic nitrogen at varying distance and direction from the pendant benzene ring and tuning its steric size, as outlined in Scheme 2B, to achieve

Scheme 2. Ligand Design To Achieve Selective Isomerization of Propargylic Esters into Dienyl Esters



regioselective and likely stereoselective synthesis of dienyl esters. This novel rational design would require the tethering of a much more basic and thereby inhibitory tertiary aliphatic amino group to a cationic Au center, which would constitute FLP if the gold catalyst could enable the intended chemistry.

Despite rearrangements of proparyglic esters[12,14] into linear dienyl esters are precedented,[15] these reactions offer structurally different products and/or, mostly notably, are limited only to scenarios in the absence of regioselectivity issues. To this end, the intended chemistry would remain to be unprecedented, let alone the development of novel gold catalysts featuring inhibitive tertiary amines (i.e., FLP).

At the outset, the propargylic ester **1a** (R = Me) was employed as substrate for the designed isomerization. We first tested the previously reported aniline ligand **L1**.[9b] As shown in Table 1, entry 1, the desired transformation did occur readily under mild conditions but with a poor regioselectivity. With this encouraging result, we implemented the ligand design shown in Scheme 2B by preparing several bifunctional ligands possessing pendent tetrahydrogenated isoquinolines, which are shown in Table 1 (see SI for their preparations). The bicyclic framework serves to minimize conformational flexibility. To our delight, with **L2** featuring a much more basic methylamino group at the same level as C3′, little inhibition of catalysis occurred, confirming the work of FLP, but the terminal diene product **3a** is only slightly more favored (entry 2) over that using **L1** as ligand. However, by replacing its methyl group with a much bigger 3-pentyl group in **L3**, **3a** was formed in 96% yield and with a pleasing selectivity of 24:1 over **2a** (entry 3). These results are consistent with the aforementioned steric preference of deprotonation at Cα over Cα' in **B**/**B′**, which is further enhanced by having Cα as a methyl group and importantly by employing **L3** possessing a bulky tertiary amino group. To our delight, the low *Z*/*E* ratio of **3a** can be substantially improved by changing the acetyl group into a bulkier pivaloyl group (entry 4). In the cases of ligands **L4** and **L5**, the basic amino groups are placed beneath C4′. As such, deprotonation at Cα' via the conformer **B′** should be preferred. This is indeed the case. As shown in entry 5, with **L4** as the ligand, the catalysis again proceeded smoothly and resulted in predominant formation of **2a** in a nearly 10-fold selectivity over **3a**. The selectivity was further enhanced by using ligand **L5**, which features the amino group even lower than **L4** (entries 6−8). The slower reaction using this ligand is attributed to intermolecular ligand amine coordination to Au(I) and hence the compromise of the frustrated nature of the Lewis pair. A good yield of **2a** was eventually achieved in the presence of 3 Å MS, at a higher temperature and after a longer period (entry 8); moreover, only its (2*E*,4*Z*)-isomer is formed. Notably,

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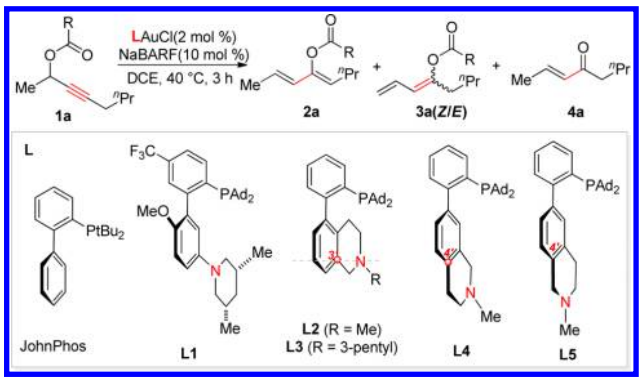
Table 1. Reaction Discovery and Ligand Optimization[a]



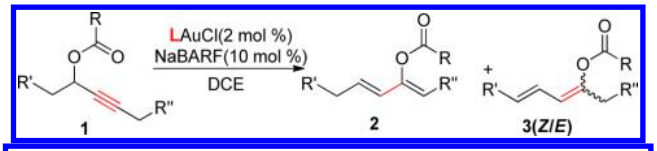
				yield[b]		
entry	R	ligand	conv[b]	2a	3a (Z/E)	4a
1	Me	**L1**	>99%	38%	64% (5.4/1)	<1%
2	Me	**L2**	>99%	28%	68% (2.8/1)	<1%
3	Me	**L3**	>99%	4%	96% (3.2/1)	<1%
4	^{t}Bu	**L3**	>99%	8%	92%[c] (12.3/1)	<1%
5	Me	**L4**	>99%	88%	9% (2.7/1)	2%
6	Me	**L5**	47%	35%	<1%	4%
7[d]	Me	**L5**	61%	49%	<1%	10%
8[e]	Me	**L5**	>99%	80%[f]	<1%	5%
9[g]	Me	JohnPhos	21%	<1%	<1%	15%
10[h]	Me	**L2**	>99%	27%	67% (3.0/1)	<1%
11[g,I]	Me	JohnPhos	28%	0%	0%	0%

[a]Reactions were performed in 1,2-dichloroethane at 40 °C for 3 h in vials, [**1**] = 0.1 M. [b]Determined by ^{1}H NMR by using 1,3,5-triisopropylbenzene as internal reference. [c]86% isolated yield. [d]40 °C for 14 h. [e]60 °C for 26 h with 3 Å MS. [f]85% isolated yield. [g]60 °C for 15 h. [h]Et_3N (4 mol %) added, and 5 mol % of NaBARF used, reaction time: 11 h. [I]5.5% Et_3N was added, 5% JohnPhosAuCl.

JohnPhos, the sterically and electronically comparable Buchwald ligand lacking any remote functionalization led to mostly slow hydration (entry 9) and little, if any, diene products. The use of basic Et_3N led to only a moderately slower reaction in the case of **L2** (2 equiv to Au, 11 h in entry 10 vs 3 h in entry 2) but shut down the formation of enone **4a** in the case of JohnPhos (1.1 equiv to Au, entry 11 vs entry 9), confirming the inhibitive nature of rather basic tertiary aliphatic amines to general gold catalysis and highlighting the frustrated nature of the our designed catalysts. Furthermore, the contrasting regioselectivities achieved with exactly the same substrate in entries 3 and 8, which is achieved by simply switching the ligand, is remarkable and not common[16] in gold catalysis. Subjecting the isolated product mixtures of these two cases to the opposite regioselectivity conditions, respectively, led to no decrease of regioisomeric ratios in either case, confirming the kinetic nature of the observed selectivities.

With the conditions optimized for both diene regioisomers, we next examined the generality of this ligand-controlled regiodivergency. The results are shown in Table 2. Similar to **1a**, propargylic esters derived from acetaldehyde (i.e., **1b**−**1d**) react smoothly, affording the internal acetoxydienes **2b**−**2d** and terminal pivaloxydienes **3b**−**3d** in excellent yields and with good to oustanding regioselectivities, respectively (entries 1−3). While the *Z*/*E* selectivities of **3b**−**3d** are moderate, only the (2*E*,4*Z*)-isomers of the internal acetoxydienes **2** are formed. Noteworthy is that the functional groups and, in particular, THP are tolerated in these reactions, highlighting the

Table 2. Scope Studies with Substrates Capable of Affording Acyloxydiene Isomers[a]



En-try	Propargylic ester **1**	Ligand conditions	dienyl ester **2/3**	Yield[b] (**2**/**3**) (3*Z*-**3**/3*E*-**3**)
1	**1b-1**, R = Me **1b-2**, R = ^{t}Bu	**L5**[c] 16 h 80 °C	**2b**	90% (>50/1) (N/A)
		L3[d] 9 h 40 °C	**3b**	94% (1/18.9) (10/1)
2	**1c-1**, R = Me **1c-2**, R = ^{t}Bu	**L5**[c,d] 7 h 60 °C	**2c**	94% (18.5/1) (N/A)
		L3[c] 6 h 40 °C	**3c**	97% (1/18.6) (6.5/1)
3	**1d-1**, R = Me **1d-2**, R = ^{t}Bu	**L5**[c,d] 12 h 60 °C	**2d**	86% (22/1) (N/A)
		L3[c] 6 h 60 °C	**3d**	98% (1/29) (5.4/1)
4	**1e-1**, R = Me **1e-2**, R = ^{t}Bu	**L**[c] 16 h 80 °C	**2e**	-
		L3[d] 10 h 60 °C	**3e**	91% (<1/50) (1.2/1)
5	**1f-1**, R = Me **1f-2**, R = ^{t}Bu	**L5**[d] 10h 40 °C	**2f**	88% (>20/1) (N/A)
		L3[c,d] 4 h 60 °C	**3f**	93% (1/1.7)[e] (12.8/1)
6	**1g**	**L2** 3 h 40 °C	**2g**	>99% (25/1)[f]
7	**1h**	**L2** 3 h 40 °C	**3h**	99% (>50/1)[f]
8	**1i**	**L2** 3 h 40 °C	**2i**	97% (20/1)[f]

[a]Reaction were carried out with LAuCl (2 mol %), NaBARF (10 mol %) in DCE (0.1 M). [b]Isolated yield. [c]LAuCl (5 mol %), NaBARF (20 mol %) were used instead. [d]3 Å molecular sieves were used. [e]The ratio of the enolic double bond. [f]The ratio of the shown product over all other isomers.

exceptionally mild nature of this isomerization chemistry. In contrast to the case of **1b** and **1c**, **1e** with its terminal hydroxy group protected by a TIPS group, no internal diene product **2e** could be generated using **L5** or other ligands, while the corresponding terminal diene **3e** is formed without accident (entry 4). The failure in the former case is likely the result of

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steric congestion caused by the bulky silyl group. With **1f** derived from 1-pentanal, the isomerization into the 2-acetoxy-1,3-diene **2f** in the presence of **L5**Au$^+$ was uneventful (entry 5); however, with **L3** as the ligand, the regioselectivity was poor, albeit in an outstanding combined yield. The use of **L2** as ligand led to similar product distribution. This outcome suggests that the increase of steric size of the propargylic substituent beyond methyl would be of limited use if 1-carboxy-1-,3-dienes of type **3** are desired. With an even bigger cyclohexyl group as the propargylic substituent, little deprotonation at the sterically congested methine site is detected (entry 6). As such, even with **L2** as the ligand, the reaction exclusively afford the 2-pivaloxy-1,3-diene **2g** in a quantitative yield. When a cyclohexyl group is installed at the alkyne terminus, the methine moiety is again too crowded to become part of the diene unit (entry 7). Consequently, the (1*Z*, 3*E*)-**3h** was formed in quantitative yield by simply using **L2** as the ligand. We also examined the enynyl acetates that could undergo the Rautenstrauch reaction in the presence of a gold catalyst.[17] To our surprise, our diene chemistry appeared to be the only observable transformation, and the trienyl ester **2i** was formed in 97% yield and with excellent geometric selectivity (entry 8). **L2** serves as a convenient ligand, and the absence of the alternative 1-acetoxy-1,3,5-triene **3i** is due to the fact that the terminal methyl hydrogens are too far away to be deprotonated.

To further explore the reaction scope, this gold catalysis is extended to propargylic esters without regioselectivity issue. As shown in Table 3, entry 1, with acetate **1j** generated from benzaldehyde the reaction proceeds with excellent yield and geometric selectivity. **L2** is again an efficient ligand. Substituents at the benzene *para* position, being electron-donating (e.g., Me, entry 2) or electron-withdrawing (e.g., CF_3, entry 3), are both tolerated, albeit the latter case requires stronger conditions, 3 Å MS and exhibits a lower yield. With an *ortho*-Br the gold catlaysis is slow but remains high yielding (entry 4). With a phenyl group at the alkyne terminus instead, **1n** also undergoes an efficient isomerization in the presence of **L2**Au$^+$, whereas the enolic C−C double bond exhibits a moderate Z/E selectivity (entry 5). Propargylic pivalates with terminal C−C triple bonds, for example, **1o**−**1s** (entries 6−10), also undergo smooth isomerization to afford 1-pivaloxy-1,3-dienes in fair to good yields and with mostly excellent (1*E*, 3*E*)-selectivity. In this case, the aniline ligand **L1** we previously developed[9b] works better than the newly developed amine ligands **L2**−**L4**. The low yield of **3o** is partly due to its volatility, and the tolerance of a cyclohexyl group in **1r** (entry 9) is noteworthy.

Two additional types of substrates exemplified by the acetates **1t** and **1u**, however, led to poor outcome (Figure 1).

Table 3. Scope Studies with Substrates without Regioselectivity Issues

entry	Propargylic ester	Ligand Conditions[a]	Product	Yield(prod/isomers)[b]
1	**1j**, R = H	**L2**, 40 °C, 1 h	**2j**, R = H	93% (>50/1)
2	**1k**, R = 4-Me	**L2**, 40 °C, 2 h	**2k**, R = 4-Me	98% (>50/1)
3	**1l**, R = 4-CF_3	**L2**, 60 °C, 15 h[c]	**2l**, R = 4-CF_3	76% (>20/1)
4	**1m**, R = 2-Br	**L2**, 40 °C, 15 h	**2m**, R = 2-Br	90% (>50/1)
5	**1n**	**L2**, 40 °C, 7 h	**3n**	92% (3.1/1)[d]
6	**1o**	**L1**, 60 °C, 15 h[c]	**3o**	56%[e] (>50/1)
7	**1p**	**L1**, 60 °C, 10 h[c]	**3p**	81% (17/1)
8	**1q**	**L1**, 60 °C, 15 h[c]	**3q**	61% (>50/1)
9	**1r**	**L1**, 60 °C, 15 h[c]	**3r**	87% (20/1)
10	**1s**	**L1**, 60 °C, 15 h	**3s**	63% (>50/1)

[a]Reactions were carried out with LAuCl (2 mol %), NaBARF (10 mol %) in DCE (0.1 M). [b]Isolated yield. [c]3 Å molecular sieves were used. [d](1*Z*)-**3n**/(1*E*)-**3n** ratio. [e]Low yield due to product volatility.

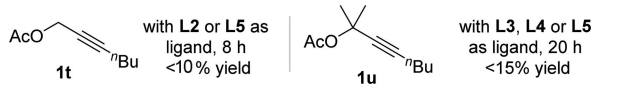
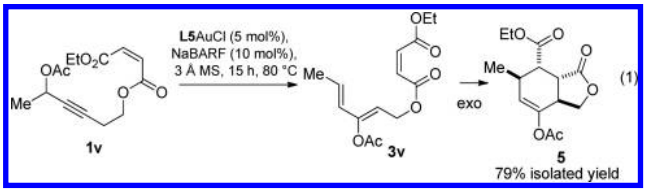


Figure 1. Poor substrates.

The potential for a rapid increase in molecular complexity by combining this dienyl ester formation with a one-pot Diels−Alder reaction is demonstrated in an intramolecular case. As shown in Scheme 3, the maleate-decorated propargyl acetate **1v**

Scheme 3. Tandem Gold Catalysis and D−A Reaction



was directly converted into the bicyclic lactone **5** under slightly elevated temperature in 79% isolated yield and with excellent *exo* selectivity.

In conclusion, rational ligand design in homogeneous gold catalysis are still much underexplored, and the application of FLP in gold chemistry has seldom been documented. In this work, we demonstrated that by strategically and rationally positioning of the remote basic tertiary amino group in the novel bifunctional biphenyl-2-ylphosphine ligands, FLP in gold catalysis is achieved, and moreover, the gold-catalyzed isomerization of propargylic esters into synthetically versatile dienyl esters can be realized under mild conditions and more importantly for substrates derived from acetaldehyde with ligand-dictated regiodivergence. The diene products are formed with good to excellent geometric selectivities in many cases. The critical importance of the remote basic amino group in the designed ligands is confirmed by the poor performance of sterically and electronically comparable and structurally related JohnPhos. It is anticipated that these ligand-enabled, gold-based FLPs will find utility in other types of gold catalysis, and the

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combination of FLP and gold catalysis should spur further advance in both areas.

■ ASSOCIATED CONTENT

Supporting Information

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Experimental procedures and compound characterization and spectra (PDF)

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Notes

The authors declare no competing financial interest.

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