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Gold(I) and Palladium(II) Complexes of 1,3,4-Trisubstituted 1,2,3-Triazol-5-ylidene "Click" Carbenes: Systematic Study of the Electronic and Steric Influence on Catalytic Activity

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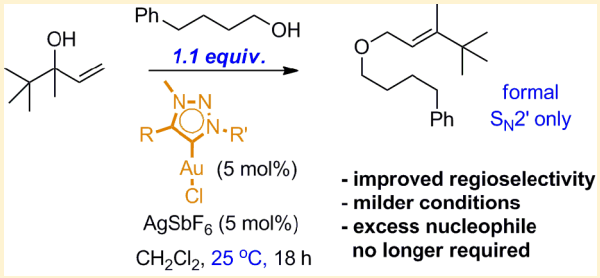
Supporting Information

ABSTRACT: The synthesis of a small family of six electronically and sterically modified 1,3,4-trisubstituted 1,2,3-triazol-5-ylidene gold(I) chloride complexes is described. Additionally, the corresponding *trans*-[$PdBr_2$(iPr_2-bimy)(1,3,4-trisubstituted 1,2,3-triazol-5-ylidene)] complexes are also generated and used to examine the donor strength of the 1,3,4-trisubstituted 1,2,3-triazol-5-ylidene ligands. All compounds have been characterized by ^1H and ^{13}C NMR and IR spectroscopy, high-resolution electrospray mass spectrometry (HR-ESI-MS), and elemental analysis. The molecular structures of four of the gold(I) and four of the palladium(II) complexes were determined using X-ray crystallography. Finally, it is demonstrated that these 1,2,3-triazol-5-ylidene gold(I) chloride complexes (Au(trz)Cl) are able to catalyze the cycloisomerization of 1,6-enynes, in high yield and regioselectivity, as well as the intermolecular direct etherification of allylic alcohols. Exploiting the Au(trz)Cl precatalysts allowed the etherification of allylic alcohols to be carried out under milder conditions, with better yield and regioselectivity than selected commercially available gold(I) catalysts.



INTRODUCTION

In the past two decades N-heterocyclic carbenes (NHCs) have become the ligands of choice for new catalyst development.[1] Initially, Arduengo-type imidazol-2-ylidene complexes[2] (**A**) dominated the area, because this class of NHC is relatively easily synthesized and handled. However, while these imidazol-2-ylidenes (**A**) and the related 1,2,4-triazol-5-ylidenes (**B**) can be readily sterically modified, the electron-donating ability of these carbenes can only be tuned over a narrow range. To overcome this limitation, a vast array of NHCs have been generated in the past 15 years, including ring-expanded carbenes (**C** and **D**),[3] cyclic alkylaminocarbenes (CAAC, **E**),[4] pyrid-2-ylidenes (**F**),[5] pyrid-4-ylidenes (**G**),[5] pyrazol-4-ylidenes (**H**),[6] and imidazol-4-ylidenes (**I**) (Figure 1a). The 1,3,4-trisubstituted 1,2,3-triazol-5-ylidenes (trz, **J**) are some of the most recent additions to the NHC family.[7] These NHCs have been termed abnormal NHCs (*a*NHC)/mesoionic carbenes (MICs) because no sensible uncharged resonance structures can be generated for these systems.[8] They have attracted considerable attention since their discovery in 2008[9] because the 1,4-disubstituted 1,2,3-triazole units, from which the *a*NHC/MICs are derived, are readily synthesized and functionalized using the modular and functional group tolerant copper(I)-catalyzed cycloaddition of azides and alkynes (CuAAC) "click" reaction.[10] Copper,[11] palladium,[12] ruthenium,[13] and iridium[14] complexes containing trz ligands have been exploited as catalysts for a wide variety of organic transformations (Figure 1b).

Recently, homogeneous gold catalysis has become an extremely popular area of research because the soft, carbophilic Lewis acidic nature of Au(I) ions enables the mild activation of unsaturated C−C bonds.[15] While much of the early work exploited phosphine-containing gold(I) complexes, the now ubiquitous N-heterocyclic carbene ligands (NHCs, **A**−**G**; Figure 1) have become increasingly popular for the generation of these types of catalysts.[16] Au(I)−NHC complexes often display enhanced stability and catalytic activity in comparison to the phosphine analogues due to the greater σ-donor strength of the carbene ligands. Because of our interest in "click" coordination chemistry,[17] we recently reported the synthesis of the Au(trz)Cl complex **7a** (Scheme 1) and showed that it was catalytically active.[18] Herein we build on this initial result and exploit the modularity of the CuAAC "click" reaction to generate a small family of sterically and electronically tuned Au(trz)Cl catalysts. Additionally, an analogous series of Pd(II) bis-carbene complexes were synthesized to enable the variation of the 1,3,4-trisubstituted 1,2,3-triazol-5-ylidene's σ-donor strength to be directly probed. Finally, the effect of this systematic modification of the Au(trz)Cl complexes is explored in two different gold(I)-catalyzed reactions: (1) the cyclo-

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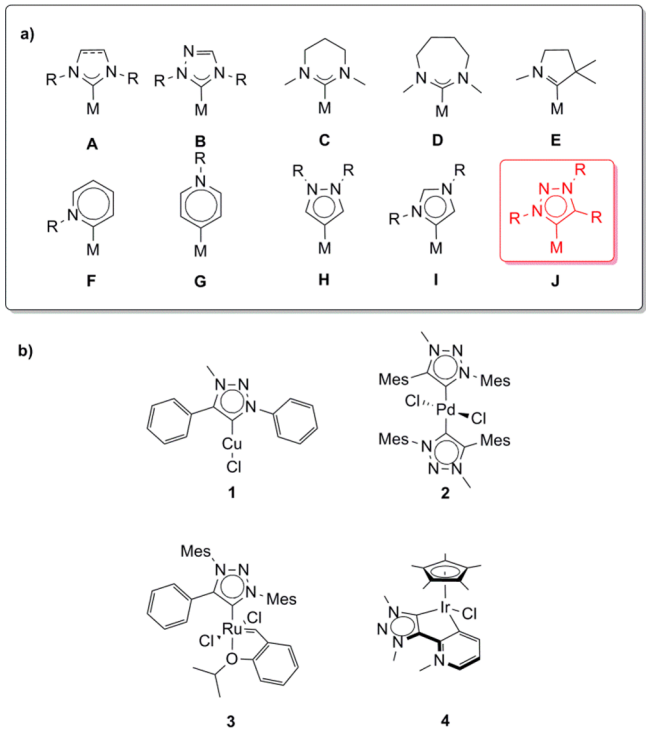


Figure 1. (a) Selected examples of generic NHC metal complexes. (b) Selected 1,3,4-trisubstituted 1,2,3-triazol-5-ylidene metal catalysts, **1**,[11d] **2**,[12i] **3**,[13d] and **4**.[14c]

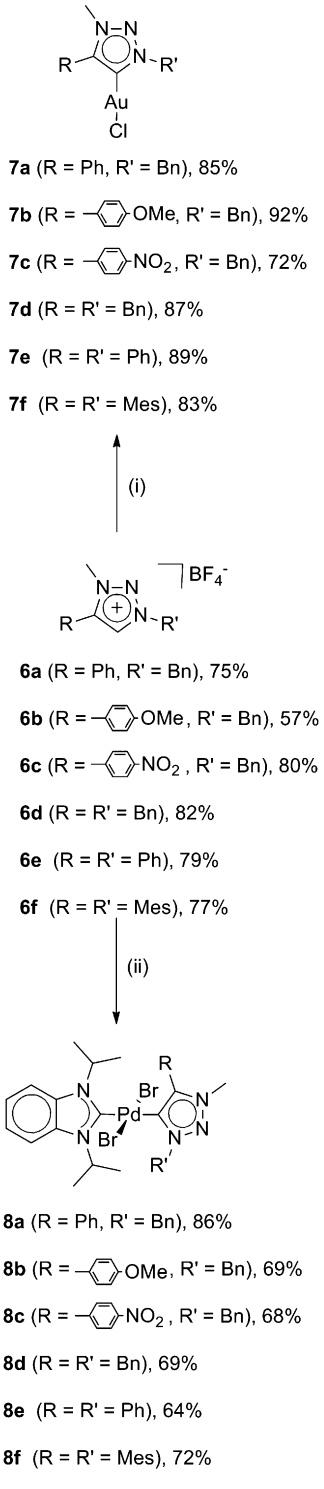
isomerization of 1,6-enynes and (2) the intermolecular direct etherification of allylic alcohols.

RESULTS AND DISCUSSION

Ligand Synthesis and Characterization. The 1,4-disubstituted-1,2,3-triazoles **5a−f**[10b,11d,19] were synthesized using previously reported methods and converted into the corresponding triazolium salts **6a−f** in good yields (57−82%) using Meerwein's reagent ($[Me_3O]BF_4$) (Scheme S1, Supporting Information.).[11d,18,20] The infrared spectra (IR) of **6a−f** confirm the presence of both the triazole unit (ν_{C-H} 3150−2965 cm^{-1}) and the BF_4^- anions (ν_{B-F} 1027−1065 cm^{-1}) in the isolated colorless materials. High-resolution electrospray mass spectra (HR-ESI-MS) of **6a−f** display signals corresponding to $[(\mathbf{6a-f}) - (BF_4^-)]^+$ and $[2(\mathbf{6a-f}) - (BF_4^-)]^+$ ions, and the proposed formulations were further supported by elemental analysis. NMR spectroscopy provided additional evidence for the formation of the triazolium salts **6a−f**, with signals due to the triazolium N-bound methyl group observed in the ^1H NMR (δ 4.0−4.5 ppm) and the ^{13}C NMR (δ 35−40 ppm) spectra, consistent with what has been previously reported.[11d,18,20b]

Gold(I) and Palladium(II) Complex Synthesis and Characterization. The gold(I) and palladium(II) trz complexes were synthesized using slight modifications of the previously reported methods, as outlined in Scheme 1. The 1,2,3-triazolium salts **6a−f** were dissolved in CH_2Cl_2/CH_3CN and treated with Ag_2O in the presence of Me_4NCl to generate the silver(I) 1,2,3-triazolylidene complexes in situ. Addition of $Au(Me_2S)Cl$ to the in situ generated silver(I) 1,2,3-triazolylidenes resulted in transmetalation and provided, after chromatography, the desired Au(trz)Cl complexes (**7a−f**; Scheme 1) as colorless or yellow (**7c**) solids in excellent yields (72−92%). The palladium complexes were also synthesized

Scheme 1[a]



[a]Legend: (i) (a) **6a−f**, Ag_2O, Me_4NCl, CH_2Cl_2/CH_3CN (1/1), room temperature, 6−14 h, (b) $Au(SMe_2)Cl$, room temperature, 2 h; (ii) (a) $[PdBr_2(i Pr_2\text{-bimy})]_2$, nBu_4NBr, $CHCl_3$, reflux, 3 h, (b) **6a−f**, Ag_2O, CH_2Cl_2, room temperature, 18 h.

using a silver(I) transmetalation protocol, as described by Huynh and co-workers,[21] and were isolated as yellow complexes (**8a−f**; Scheme 1) with the formula *trans*-$[PdBr_2(iPr_2\text{-bimy})(trz)]$ (where iPr_2-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene) in good to excellent yields (64−86%). These gold(I) and palladium(II) compounds were

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characterized by elemental analysis, HR-ESI-MS, IR, and ^{1}H and ^{13}C NMR spectroscopy. The elemental analyses of the complexes were consistent with the proposed formulations, and this was further supported by HR-ESI-MS. The gold complexes **7a−f** display major signals due to $[Au(trz)Cl + Na]^+$, $[Au(trz) - Cl - Au(trz)]^+$ and $[Au(trz)_2]^+$ ions, while the palladium complexes show major peaks consistent with $[PdBr(iPr_2\text{-bimy})(trz)]^+$, $[PdCl(iPr_2\text{-bimy})(trz)]^+$, and $[PdBr_2(iPr_2\text{-bimy})(trz) + Na]^+$ (Supporting Information). The ^{1}H NMR spectra of **7a−f** and **8a−f** were also consistent with complex formation. The ^{1}H NMR spectra of the triazolium salts **6a−f** contain a C_{trz}−H proton signal between 7.5 and 9.0 ppm which is absent in the spectra of the metal complexes (**7a−f** and **8a−f**), indicative of deprotonation and carbene formation.[7,18,21] Additionally, the signals due to the *N*-methyl protons of the triazole units experience an upfield shift on complex formation. In the complexes with phenyl substituents the *o*-phenyl proton signals undergo a downfield shift, due to the proximity of the deshielding metal centers. The ^{13}C NMR spectra of the complexes display 1,3,4-trisubstituted 1,2,3-triazol-5-ylidene carbon signals at ∼160 ppm, consistent with previous studies.[7,18,21]

The molecular structures of four of the gold complexes (**7b−d,f**; Figure 2, Table 1, and the Supporting Information) were determined using X-ray crystallography.[22] The crystals were grown via vapor diffusion of either diethyl ether or petroleum ether into a dichloromethane solution of one of the complexes. The Au(I) ions of the complexes are bound to a 1,3,4-trisubstituted 1,2,3-triazol-5-ylidene and a chloride ligand in the expected linear fashion (C−Au−Cl bond angles range from 176.3 to 178.8°). The Au−C_{trz} (1.972−2.001 Å) and Au−Cl (2.272−2.298 Å) bond lengths are similar to those observed in other gold(I) triazolylidene complexes.[7a,e,18,22,23]

The extended solid-state structure of complex **7b** contains dimers (Supporting Information) that are held together by weak hydrogen-bonding interactions between the methoxy oxygen atom and the aryl proton situated ortho to the methoxy group of the adjacent molecule (C−H···O = 2.690(3) Å, C···O = 3.592(6) Å). Additionally, $\pi-\pi$ interactions are observed between the triazole ring and the six-membered methoxyphenyl ring (centroid···centroid = 3.748 Å).

In the extended structures of **7c,d** the complexes form antiparallel dimers (Supporting Information). The **7c** dimer is stabilized by Cl···π interactions (Cl···centroid = 3.377, 3.668 Å). In the case of **7d**, the dimer motif extends throughout the crystal lattice as a double-stranded, one-dimensional supramolecular polymeric chain. The strands of the chain are connected via weak[24] C−H···Cl hydrogen bonding of the methyl group of the triazole ring to the chloride of the adjacent molecule (H···Cl = 2.686(2) Å, C···Cl = 3.537(1) Å), as well as C−H···π interactions between the acidic benzylic protons and the six-membered ring (centroid···H = 2.737 Å, centroid···C = 3.558 Å). The adjacent strands of the chains are connected by Cl···π bonding (**7d**, 3.469 Å) between the chloride and the electron-poor triazole ring.[25]

The structure of **7f** also displays dimers that are assembled through weak hydrogen-bonding interactions between the unsubstituted N2 nitrogen and the *N*-methyl proton of the adjacent molecule (C−H···N = 2.673(6) Å, C···N = 3.52(1) Å). The chloride ligands of these molecules also hydrogen bond with the *N*-methyl proton of another molecule in the lattice (H···Cl = 2.743(2) Å, C···Cl = 3.556(9) Å).

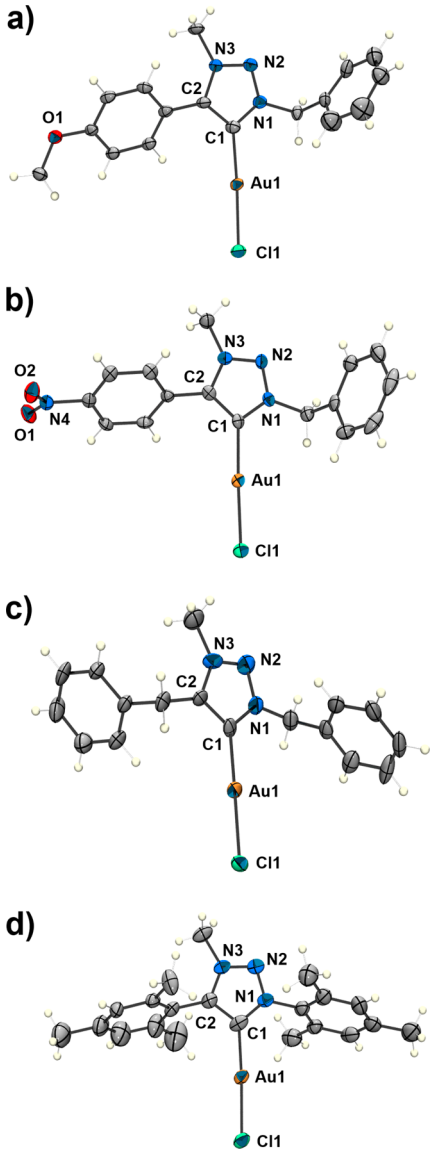

Figure 2. ORTEP[27] diagrams of the gold(I) complexes (a) **7b**, (b) **7c**, (c) **7d**, and (d) **7f**. The thermal ellipsoids are shown at the 50% probability level. The benzyl group of **7b** is disordered, but for clarity, only one orientation is shown.

Table 1. Selected Bond Distances (Å) and Angles (deg) of the Gold(I) Complexes 7a−d,f

	7a[18]	7b	7c	7d	7f
Au1−C1	1.982(4)	1.979(5)	1.986(5)	2.001(9)	1.974(8)
Au1−Cl1	2.294(1)	2.292(2)	2.272(1)	2.298(2)	2.284(2)
C2−C1−N1	103.1(3)	102.9(5)	103.2(5)	104.4(8)	103.2(7)
C1−Au1−Cl1	177.2(1)	176.3(2)	178.8(2)	178.6(3)	177.1(2)

Surprisingly, no aurophilic interactions are observed in any of the structures (**7a**[18] or **7b−d,f**); the shortest gold···gold distance (**7d**, Au−Au = 3.612 Å)[26] is greater than the sum of the van der Waals radii of two Au(I) centers (3.60 Å).

Four of the palladium complexes, **8a−d**, were also characterized by X-ray crystallography (Figure 3, Table 2, and the Supporting Information). All complexes crystallize in a *trans* square-planar geometry and are essentially isostructural (Figure

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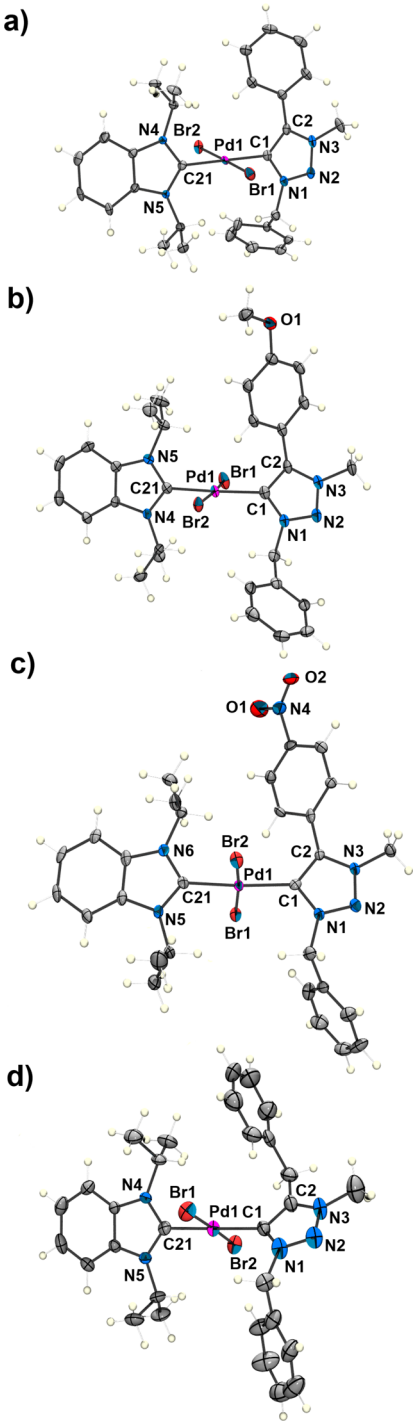

Figure 3. ORTEP[27] diagrams of the palladium(II) complexes (a) **8a**, (b) **8b**, (c) **8c**, and (d) **8d**. The thermal ellipsoids are shown at the 50% probability level. The trz ligand of **8d** is disordered, but for clarity, only one orientation is shown.

3) with those previously reported.[21] The bromide ligands sit orthogonal to the plane of the heterocycles to minimize steric interactions. The complexes **8a**–**d** have acute C2–C1–N1 angles of 101–103° (Table 2) which are similar to those of **7a**–**d**,**f** (Table 1) and consistent with what has been observed previously for 1,2,3-triazolylidenes.[7,10] The bromide ligands of the complexes angle toward the benzimidazolylidyl carbene carbon, due to back-donation from the bromide ligand to the empty *p* orbital of the carbon (C_{bimy}–Br = 3.048(3)–3.147(5) Å; C–Br(VDW) = 3.55 Å).[21,28] Additionally, this is supported by the shorter C21–Pd1 bond length in comparison to the triazolylidyl C1–Pd1 bond (Table 2). The "unusual" interaction of the tertiary isopropyl hydrogens and the palladium center, previously discussed by Huynh,[25,32] is also present in the structures (Pd···H–C = 2.6592(2)–2.7738(4) Å).

Table 2. Selected Bond Distances (Å) and Angles (deg) of Palladium(II) Complexes 8a–d

	8a	8b	8c	8d
Pd1–C1	2.040(5)	2.050(2)	2.046(5)	2.04(2)
Pd1–C21	2.015(5)	2.001(2)	2.007(4)	2.015(5)
C1–Pd1–C21	179.5(2)	177.86(9)	175.9(2)	179.3(6)
C2–C1–N1	102.3(4)	102.6(2)	102.2(4)	101.0(2)
N4–C21–N5	107.4(4)	107.6(2)	107.4(4)	107.1(4)
Br1–Pd1–Br2	176.50(2)	173.54(1)	173.49(2)	177.1(2)
C2–C1–C21–N4	7.6(6)	2.0(3)	1.2(6)	40.0(2)

Complexes **8a**–**c** form 1-D supramolecular polymeric tapes (Supporting Information) that are assembled through offset face-to-face π–π interactions between the 1,3,4-trisubstituted 1,2,3-triazol-5-ylidene ring and the benzene ring of the benzimidazolylidene ligand of an adjacent molecule (centroid···centroid distances range from 3.709 to 3.896 Å). The complex **8d** also extends into 1-D supramolecular ribbons (Supporting Information). These ribbons are supported by C–H···π interactions between the benzylic protons of the C substituent and the N-bound benzyl group of an adjacent molecule (C–H3···C17 = 2.82(1) Å, C3···C17 = 3.75(2); C–H3···C16 = 2.90(1) Å, C3···C16 = 3.94(1) Å), as well as C–H···Br interactions between the C-bound benzyl group and a bromide ligand of an adjacent molecule (C–H8···Br1 = 2.873(8) Å, C8···Br1 = 3.78(1) Å).

Ligand Donor Properties. The mild CuAAC "click" methodology used to generate the 1,3,4-trisubstituted 1,2,3-triazol-5-ylidene ligands potentially provides a facile way to tune both steric and electronic properties of the resulting carbene complexes. The M–C_{trz} bond lengths (Tables 1 and 2) were examined to see if there is a correlation between the electronic nature of the trz ligand and the metal–carbene bond length in the solid-state upon side-arm (wingtip) substitution of the compounds **7a**–**f** and **8a**–**f**. The Au–C_{trz} bond lengths of the gold(I) complexes **7b** (Aryl-OMe) < **7a** (Aryl-H) < **7c** (Aryl-NO_2) follow the expected trend with the more electron rich methoxy-substituted complex **7b** displaying a shorter Au–C_{trz} bond than the parent complex **7a**. Similarly, the electron-poor nitro-substituted complex **7c** has a longer Au–C_{trz} bond than the parent complex **7a**. However, the observed differences are of a similar magnitude to the experimental uncertainty (Table 1). The correlation breaks down with complexes **7d**,**f**, where the observed Au–C_{trz} bond lengths are longer (**7d**) and shorter (**7f**) than would be predicted on the basis of inductive arguments. Furthermore, the Pd–C_{trz} bond lengths for complexes **8a**–**d** are all essentially identical within the experimental uncertainty (Table 2). Therefore, there is no obvious correlation between the observed M–C_{trz} bond lengths in the solid-state and the electronic nature of the trz ligand. However, it is noted that the M–C distance can be affected by other parameters such as crystal-packing effects.

As the solid-state data provided no useful information on the donor strengths of the various trz ligands, the ^{13}C NMR spectra of palladium complexes **8a**–**f** were used to provide insight into

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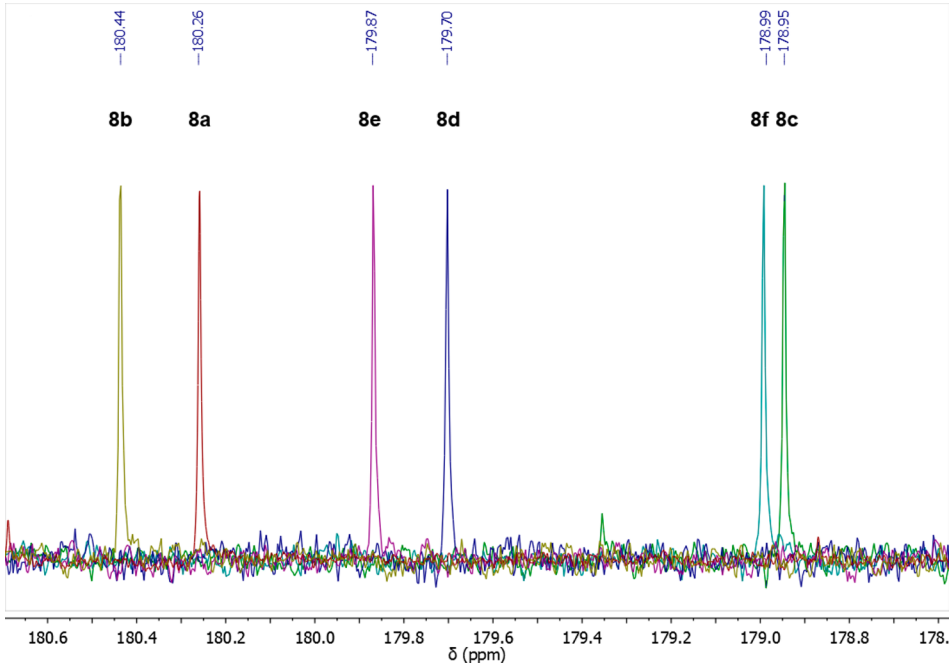

Figure 4. Superimposed ^{13}C NMR spectra ($CDCl_3$, 298 K) showing the reporter benzimidazol-2-ylidene carbon signals of **8a**–**f**. The data are referenced to 77.16 ppm,[29] not 77.7 ppm as reported in the original Huynh papers.[21,27]

the ligand's donor properties. Huynh and co-workers previously showed that these benzimidazol-2-ylidene–dibromopalladium(II) complexes can be used to probe the σ-donor strength of the ligands *trans* to the benzimidazol-2-ylidene.[21,28] They have found that there is a direct relationship between σ-donor strength of the *trans* ligand and the chemical shift of the benzimidazole carbene carbon in the ^{13}C NMR spectra of the dibromopalladium(II) complexes.[21,28] Additionally, this system has previously been used to show that the mesoionic trz ligands are stronger donors than imidazol-2-ylidenes.[21]

The ^{13}C NMR spectra of palladium complexes **8a**–**f** were obtained in $CDCl_3$ solution at 298 K. Consistent with what Huynh and co-workers previously reported,[21] the benzimidazol-2-ylidene reporter peaks were observed at approximately 180 ppm (Figure 4).

The parent palladium(II) complex **8a** displays the peak for the benzimidazolylidene carbon at 180.26 ppm. Consistent with expectations, the benzimidazolylidene carbon signal of the more electron-rich methoxy-substituted complex **8b** has shifted downfield (δ 180.44 ppm), relative to the ligand in **8a**, suggesting that the 4-$MeOC_6H_5$-trz ligand is more electron donating that the parent Ph-trz ligand. Similarly, the reporter carbon of the nitro-substituted complex **8c** is observed upfield (δ 178.95 ppm) relative to **8a**, indicating that the presence of the electron-withdrawing functionality reduces the trz ligand's donor properties, consistent with expectation. Replacing the benzyl substituent of the parent with a phenyl ring generating the diphenyl-substituted complex **8e** also leads to a reduction of the trz ligand σ-donor strength (δ 179.87 ppm), as is expected upon the removal of the electron-donating methylene linker.

The observed positioning of the benzimidazolylidene reporter carbon signals in the dibenzyl-substituted complex **8d** (δ 179.70 ppm) and the dimesityl-substituted complex **8f** (δ 178.99 ppm) was unexpected. The data suggest that these ligands are weaker σ donors than would be expected on the basis of electronic arguments. Changing the phenyl substituent of the parent complex (**8a**) to a benzyl in **8d** would be expected to lead to an increase in the electron-donating properties of the trz-d ligand due to the presence of a second inductively donating methylene group. Likewise, the presence of the three methyl groups on the mesityl substituents of complex **8f** should make this trz-f ligand more electron-donating than the structurally similar diphenyl-trz-e. The observed ^{13}C shifts of **8a**,**e** suggest that the trz ligands in complexes **8d**,**f** are weaker σ donors than trz-a and trz-e. As the substituents on the trz ligand of **8d**,**f** are larger (bulkier) than those on the other examples, it is postulated that steric effects lead to this observed weakening of the σ-donor properties. ^1H NMR spectroscopic and X-ray crystallographic data provide some support for this theory. The ^1H NMR spectra of all palladium complexes show characteristic septet signals representing the two tertiary proton signals of the benzimidazolylidene isopropyl groups. In most cases we see no separation of these signals, indicative of freely rotating ligands in solution. The exception is **8d**, which displays two distinct signals for the isopropyl groups indicative of hindered rotation about the Pd–trz bond, presumably due to steric factors. In addition to this, the solid-state structures of **8a**–**c** have a coplanar arrangement of the heterocyclic ligands, whereas in **8d** the aforementioned ligands twist out of this plane (C2–C1–C21–N4 = 40.0(2)°). Although the solid-state structure of **8f** was not obtained, molecular models (Supporting Information) show the presence of steric clashes that could weaken interaction of trz-f with the Pd(II) ion. While not completely as expected, these results indicate that electronic alteration of the side-arm substituents (wingtip groups) does affect the donor properties of the trz ligands and suggests that CuAAC "click" chemistry could be exploited to modulate these properties in a facile fashion.

Catalysis with Gold(I) 1,3,4-Trisubstituted 1,2,3-Triazol-5-ylidene Complexes. With the family of new Au(trz)Cl complexes **7a**–**f** in hand, we were keen to investigate their application in catalysis. In particular, we wished to observe what effect, if any, changing the substituents on the triazolylidene ligand would have on catalysis. Thus, the enyne

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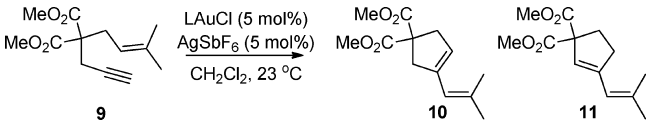
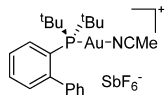
9 was subjected to skeletal rearrangement[30] catalyzed by various Au(trz)Cl precatalysts—a typical test reaction for catalytic activity of new gold complexes[31] (Table 3). Our initial

Table 3. Screen of 7a–f as Precatalysts in the Skeletal Rearrangement of 9



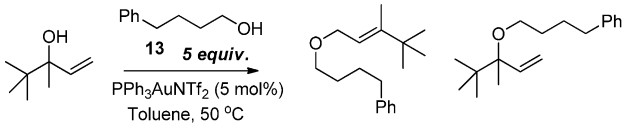
Entry	LAuCl	Time (min)	10:11[a]	Yield (%)[b]
1	**7a**	15	1:2	42[c]
2	**7b**	15	1:2	45[c]
3	**7d**	15	1:2	50[c]
4	**7e**	15	1:2	47[c]
5[e]	**7a**	1	>20:1	92[d]
6	**7b**	1	20:1	94[d]
7	**7c**	1	>20:1	95[d]
8	**7d**	1	13:1	93[c]
9	**7e**	1	>20:1	72[d]
10[f]	**7f**	1	>20:1	98[d]
11[g]	**7f**	1	>20:1	93[d]
12[g]	PPh_3AuCl	25	**10**[h]	91[31h]
13[g,i]		5	**10**[h]	98[31h]

[a]Determined by ^1H NMR analysis. [b]Isolated yields. [c]Mixture of **10** and **11** as indicated. [d]**10** only. [e]Same result if AgCl precipitate is filtered out prior to reaction with **9**. [f]Full conversion even with mercury drop test. [g]2 mol % catalyst. [h]Ratio not reported. [i]$AgSbF_6$ not added.

few results were rather disappointing, as they showed poor selectivities, poor yields, and (within error) fairly similar results (entries 1–4). However, suspecting that **11** may form from **10** over time, the reactions were repeated with a much shorter reaction time (1 min vs 15 min before), and to our delight, the selectivities and yields improved significantly (entries 5–10). Electronic tuning seems to do little to the catalytic activity: the parent Bn,Ph-substituted Au(trz)Cl **7a** reacts with almost the same excellent selectivity and yields (entry 5) as the electron-rich (**7b**, entry 6) and electron-poor (**7c**, entry 7) versions. Next, the effect of sterics around the trz was probed. Changing from the parent Bn,Ph-substituted trz **7a** to the more flexible dibenzyl-substituted **7d** (entry 8) causes a drop in selectivity (13:1 vs >20:1) but not yield (93% vs 92%). Having diphenyl substitution (**7e**, entry 9) retains the excellent >20:1 selectivity but causes a drop in yield (72%). Finally, the more hindered dimesityl-substituted **7f** provides the best result in this series, with an excellent 98% yield and >20:1 selectivity of **10**:**11**. Therefore, it seems that for the skeletal rearrangement **9** → **10**, steric tuning on the trz ligand has more influence than electronic tuning. Increased steric protection around the Au center provided by the Mes substituents in **7f** appears to be beneficial for the performance of the catalyst in this test reaction. As a control, the reaction in entry 5 was also repeated with the AgCl filtered out of the mixture of Au(trz)Cl **7a** and $AgSbF_6$, prior to introduction of **9** in order to ensure that the silver is not playing a crucial role in the reaction.[32] The reaction behaves in exactly the same manner regardless of the presence or absence of AgCl in the reaction, confirming that silver is not playing a significant role in this reaction. A mercury drop test[33] was also carried out on the reaction shown in entry 10, resulting in full conversion, suggesting that the catalytic activity is not due to the formation of heterogeneous nanoparticles. Finally, reducing the catalyst loading to 2 mol % still produces an excellent 93% yield within 1 min (entry 11) and shows that it compares favorably with results from commonly used gold catalysts (entries 12 and 13).

Next, we were keen to demonstrate the utility of the Au(trz)Cl complexes as precatalysts in a reaction developed within one of our laboratories. We have previously shown that direct allylic etherification using unactivated allylic alcohols and alcohol nucleophiles is possible using gold catalysis (e.g., Scheme 2).[34] The original method requires excess (5 equiv) of

Scheme 2. Example of Previous Conditions for Direct Allylic Etherification



the alcohol nucleophile (e.g., **13**) for best results, using $Au(PPh_3)NTf_2$ as the catalyst.[15e,35] An excess of **13** is to ensure that the allylic alcohol **12** does not react with itself and also to improve selectivity under these conditions. To our delight and surprise, using the new Au(trz)Cl complexes **7a–f** as precatalysts allows not only for a significant reduction in the amount of alcohol nucleophile to 1.1 equiv but also for the reaction to be carried out at a much milder room temperature (vs. 50 °C, Table 4), thus greatly improving on the original conditions shown in Scheme 2.

As shown in Table 4, all the Au(trz)Cl precatalysts **7a–f** screened (entries 1–6) provide good yields of the desired product **14** in excellent regioselectivities (>20:1 of **14**:**15** vs 12:1 using the original conditions in Scheme 2) using only 1.1 equiv of the alcohol nucleophile **13** and a mild 25 °C. Unlike the enyne skeletal rearrangement reaction shown in Table 3, the allylic etherification reaction is sensitive to electronic tuning on the trz ligand (entries 1–3). Changing from the parent precatalyst **7a** (entry 1) to the more electron rich **7b** (entry 2) gives a slightly improved yield and *E*:*Z* selectivity, while the more electron-withdrawing **7c** shows a noticeably lower yield of **14** (entry 3). Tuning the sterics around the trz ligand (entries 4–6) does not really seem to affect the yield of **14** or the regioselectivity. Next, we were keen to see how Au(trz)Cl precatalysts **7a–f** compare with other commonly used gold(I) catalysts (entries 7–10). Using the original catalyst $Au(PPh_3)NTf_2$[36] under these conditions results in incomplete conversions and poor selectivities, including at least 9% of self-reaction of **12** (entry 7). The commercially available NHC precatalysts Au(IPr)Cl and Au(IMes)Cl were also investigated for comparison purposes (entries 8 and 9). $Au(IPr)SbF_6$, like $Au(PPh_3)NTf_2$, results in poor selectivities and conversions (entry 8). $Au(IMes)SbF_6$, on the other hand, provides a good yield of **14** although the *E*:*Z* selectivity is poorer than with

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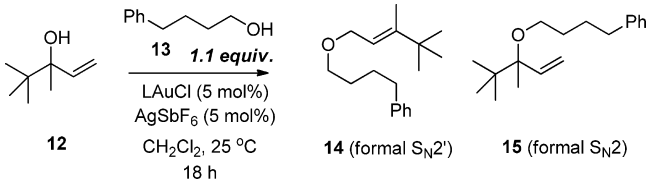
Table 4. Direct Allylic Etherifications using Au(trz)Cl (7a–f) as Precatalysts



entry	LAuCl	14:15[a]	yield of 14, %[b]	E:Z[a]
1	**7a**	>20:1	74	6:1
2	**7b**	>20:1	76	8:1
3	**7c**	>20:1	64	8:1
4	**7d**	>20:1	67	9:1
5	**7e**	>20:1	67	12:1
6	**7f**	>20:1	66	6:1
7	$Au(PPh_3)NTf_2$	4:1	incomplete reaction:[c,d] 3:4:1 **12:14:15** 9% self-reaction of **12**	5:1
8	Au(IPr)Cl	2.5:1	incomplete reaction:[c] 3:2.5:1 **12:14:15**	4:1
9	Au(IMes)Cl	>20:1	70	5:1
10	$Au(PPh_3)Cl$	17:1	61	4:1

[a]Determined by ^{1}H NMR analysis. [b]Isolated yields of **14**. [c]Using 2,3,5,6-tetrachloronitrobenzene as internal standard. [d]No $AgSbF_6$ added.

$Au(trz)SbF_6$ (entry 9). Finally, the phosphine counterpart $Au(PPh_3)SbF_6$ provides poorer yields as well as selectivities (entry 10) than the $Au(trz)SbF_6$ catalysts.

CONCLUSION

In summary, the gold(I) complexes **7a–f** and palladium(II) complexes **8a–f** have been synthesized and characterized through a combination of ^{1}H and ^{13}C NMR and IR spectroscopy, HR-ESI-MS, and elemental analysis. The molecular structures of four of the gold(I) and four of the palladium(II) complexes were determined using X-ray crystallography. The σ-donor strength of the trz ligands **a–f** has been assessed using the palladium(II) probe complexes **8a–f**. These measurements confirm that that electronic and steric alteration of the side-arm substituents (wingtip groups) does effect the donor properties of the trz ligands and suggests that CuAAC "click" chemistry could be exploited to modulate these properties in a facile fashion. The gold(I) complexes **7a–f** have been used as efficient precatalysts for both the enyne skeletal rearrangement reaction (Table 3) and the direct allylic etherification reaction (Table 4). In the former, steric tuning on the trz ligand seemed to improve yields, whereas the latter is more sensitive to electronic tuning. Therefore, it is useful to have a facile and modular method (via the CuAAC "click" reaction) toward these Au(trz)Cl complexes in order to have access to a range of these complexes for catalyst screening. Pleasingly, the Au(trz)Cl complex **7b** also outperforms a range of commonly used commercially available gold(I) precatalysts in the allylic etherification reaction (Table 4) and allows for the procedure to be greatly improved (Table 4 vs Scheme 2).

EXPERIMENTAL SECTION

General Considerations. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification. Petroleum ether is the fraction boiling in the range 40–60 °C, CH_3CN refers to acetonitrile, and CH_2Cl_2 is dichloromethane. All melting points were determined using a Mettler-Toledo FP62 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian 400 MR or a Varian 500 VNMRS spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm) and referenced to residual solvent peaks ($CDCl_3$, ^{1}H δ 7.26 ppm, ^{13}C δ 77.16 ppm; CD_3CN, ^{1}H 1.94, ^{13}C 1.32, 118.26 ppm). Coupling constants (J) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: m = multiplet, spt = septet, quint = quintet, q = quartet, t = triplet, d = doublet, s = singlet, br = broad. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer with an attached ALPHA-P measurement module. Microanalyses were performed at the Campbell Microanalytical Laboratory at the University of Otago. High-resolution electrospray mass spectrograms (HR-ESI-MS) were collected on a Bruker micro-TOF-Q spectrometer.

The 1,2,3-triazoles 1-benzyl-4-phenyl-1*H*-1,2,3-triazole (**5a**),[17e] 1-benzyl-4-(4-methoxy)phenyl-1*H*-1,2,3-triazole (**5b**),[19c] 1-benzyl-4-(4-nitro)phenyl-1*H*-1,2,3-triazole (**5c**),[37] 1,4-dibenzyl-1*H*-1,2,3-triazole (**5d**),[19b] 1,4-diphenyl-1*H*-1,2,3-triazole (**5e**),[19a] and 1,4-dimesityl-1*H*-1,2,3-triazole (**5f**),[11d] the triazolium compounds **6a**,[18] **6b**,[20b] and **6e,f**,[11d] and the complexes **7a**[18] and **8a**[21] were synthesized using slightly modified literature procedures.

The gold(I)-catalyzed reactions were carried out without the need for dry solvents or inert atmosphere. However, $AgSbF_6$ was stored and weighed out in a glovebox as a precaution to avoid hydrolysis to the corresponding Brønsted acid in our screening experiments.

Synthesis of Triazolium 6c. 1-Benzyl-4-(4-nitrophenyl)-1*H*-1,2,3-triazole (**5c**; 174 mg, 0.619 mmol, 1.0 equiv) was added to a Schlenk flask, which was then evacuated and back-filled with argon three times. Dry dichloromethane (CH_2Cl_2, 50 mL) was added, and the solution was bubbled with argon for 5 min before $[Me_3O]BF_4$ (164 mg, 1.11 mol, 1.8 equiv) was added. The suspension was stirred under argon for 2 days. MeOH (2 mL) was added, and the solvent was removed under reduced pressure, resulting in the formation of a brown oil which was stirred in petroleum ether (50 mL) for 2 days. The product was isolated as a yellow powder by filtration (189 mg, 80%). Mp: 176 °C dec. IR: ν (cm^{-1}) 3157, 3137, 3109, 3081, 3015, 2967, 1602, 1576, 1528, 1490, 1457, 1445, 1430, 1357, 1318, 1290, 1195, 1162, 1065 (br), 1054 (br), 1023, 853, 750, 718, 706, 683, 623, 578, 560, 520, 474, 460. ^{1}H NMR (400 MHz, CD_3CN): δ 8.59 (s, 1H, H_c), 8.41 (d, J = 8 Hz, 2H, H_a), 7.84 (d, J = 8 Hz, 2H, H_b), 7.53 (m, 2H, H_e), 7.49 (m, 3H, $H_{f/g}$), 5.80 (s, 2H, H_d), 4.19 (s, 3H, H_h). ^{13}C NMR (100 MHz, CD_3CN): δ 150.79, 142.64, 132.85, 132.10, 130.80, 130.34, 130.30, 130.26, 129.34, 125.37, 58.30, 39.88. HR-ESI-MS: m/z 677.2443 [2(**6c**) − BF_4^-]$^+$ (calcd for $C_{32}H_{30}BF_4N_8O_4$ 677.2419), 295.1194 [**6c** − BF_4^-]$^+$ (calcd for $C_{16}H_{15}N_4O_2$ 295.1195). Anal. Calcd for $C_{16}H_{15}BF_4N_4O_2$: C, 50.29; H, 3.96; N, 14.66. Found: C, 50.55; H, 4.06; N, 14.47.

Synthesis of Triazolium 6d. 1-Benzyl-4-benzyl-1*H*-1,2,3-triazole (**5d**; 358 mg, 1.44 mmol, 1.0 equiv) was added to a dry Schlenk flask, which was then evacuated and back-filled three times. Dry CH_2Cl_2 (50 mL) was added, and the solution was bubbled with argon for 5 min. $[Me_3O]BF_4$ (451 mg, 3.05 mmol, 2.1 equiv) was added, and the suspension was stirred under argon for 3 days. The reaction was quenched with MeOH (3 mL), and the solvent was removed under reduced pressure to give a brown oil. Diethyl ether (50 mL) was added to the oil and consequently stirred for 2 h, resulting in the formation of a white precipitate. The product was isolated by filtration as a white solid (415 mg, 82%). Mp: 125 °C dec. IR: ν (cm^{-1}) 3124, 3070, 3038, 2991, 1607, 1585, 1499, 1454, 1384, 1361, 1315, 1210, 1175, 1157, 1027 (br), 760, 730, 704, 692, 645, 522, 479, 456. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (s, 1H, H_e), 7.45–7.43 (m, 2H, H_g), 7.40–7.39 (m, 3H, $H_{h/i}$), 7.32 (t, J = 10 Hz, 2H, H_b), 7.27 (t, J = 10 Hz, 1H, H_a) 7.23 (d, J = 10 Hz, 2H, H_c), 5.63 (s, 2H, H_d) 4.19 (s, 2H, H_f), 4.09 (s, 3H, H_j). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.18, 132.97, 131.20, 130.12, 129.66, 129.62, 129.51, 129.04, 128.92, 128.24, 57.65, 38.05, 29.44. HR-ESI-MS: m/z 615.2033 [2(**6d**) − BF_4^-]$^+$ (calcd for $C_{34}H_{36}BF_4N_6$ 615.3031), 264.1533 [**6d** − BF_4^-]$^+$ (calcd for $C_{17}H_{18}N_3$ 264.1495). Anal. Calcd for $C_{17}H_{18}BF_4N_3$: C, 58.15; H, 5.17; N, 11.97. Found: C, 58.16; H, 5.17; N, 12.00.

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Synthesis of Au(I) Complex 7b. To a solvent mixture of CH_2Cl_2 and CH_3CN (1/1, 10 mL) were added **6b** (0.142 mg, 0.387 mmol, 1.0 equiv), tetramethylammonium chloride (43 mg, 0.392 mmol, 1.0 equiv), and Ag_2O (45 mg, 0.194 mmol, 0.5 equiv), and the contents of the foil-covered reaction flask were stirred for 5 h. $Au(SMe_2)Cl$ (0.115 g, 0.391 mmol, 1.0 equiv) was added, and the resulting mixture was stirred for 2 h. The mixture was filtered through a Celite plug (CH_2Cl_2) and the solvent removed under reduced pressure to give a brown oil. The product was purified by vapor diffusion of a concentrated CH_2Cl_2 solution with diethyl ether to obtain a brown oil, which was added dropwise to stirred petroleum ether to give a white solid (185 mg, 92%), which was isolated by filtration. Mp: 155 °C dec. IR ν (cm^{-1}) 3064, 3026, 2968, 2937, 2908, 2833, 1613, 1577, 1546, 1488, 1457, 1438, 1395, 1363, 1296, 1256, 1178, 1115, 1088, 1072, 1020, 845, 836, 820, 793, 748, 734, 702, 656, 617, 599, 571, 513, 459. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63−7.61 (m, 2H, H_e), 7.55 (d, J = 8 Hz, 2H, H_c), 7.42−7.38 (m, 3H, $H_{f/g}$), 6.99 (d, J = 8 Hz, 2H, H_b), 5.66 (s, 2H, H_d), 4.05 (s, 3H, H_h), 3.85 (s, 3H, H_a). ^{13}C NMR (100 MHz, $CDCl_3$): 161.18 (s, $C_{carbene}$), 157.54, 147.16, 13.79, 131.09, 129.28, 129.21, 129.12, 118.23, 114.73, 59.13, 55.58, 37.86. HR-ESI-MS: m/z 987.1759 [Au(trz-b)-Cl-Au(trz-b)]$^+$ (calcd for $C_{34}H_{34}Au_2ClN_6O_2$ 987.1763), 755.2396 [Au(trz-b)$_2$]$^+$ (calcd for $C_{34}H_{34}Au_2N_6O_2$ 755.2409), 534.0626 [**7b** + Na]$^+$ (calcd for $C_{17}H_{17}AuClN_3NaO$ 534.0623), 280.1438 [**6b** − BF_4]$^+$ (calcd for $C_{17}H_{18}N_3O$ 280.1450). Anal. Calcd for $C_{17}H_{17}AuClN_3O$: C, 39.90; H, 3.35; N, 8.21. Found: C, 39.96; H, 3.25; N, 8.19.

Synthesis of Au(I) Complex 7c. To a solvent mixture of CH_2Cl_2 and CH_3CN (1/1, 10 mL) were added **6c** (217 mg, 0.568 mmol, 1.2 equiv), tetramethylammonium chloride (63 mg, 0.575 mmol, 1.2 equiv), and Ag_2O (73 mg, 0.315 mmol, 0.7 equiv), and the contents of the foil-covered reaction flask were stirred for 7 h. $Au(SMe_2)Cl$ (0.138 g, 0.469 mmol, 1.0 equiv) was added, and the resulting mixture was stirred for 3 h. The mixture was filtered through a Celite plug (CH_2Cl_2), and the solvent was removed under reduced pressure to give a yellow oil, which was purified by column chromatography (9/1 CH_2Cl_2/acetone). A concentrated CH_2Cl_2 solution of the product was crystallized via vapor diffusion of diethyl ether to produce bright yellow crystals (172 mg, 72%). Mp: 170 °C dec. IR: ν (cm^{-1}) 3084, 2925, 2858, 1601, 1520, 1516, 1498, 1479, 1454, 1435, 1341(br), 1287, 1165, 1106, 1091, 1076, 1044, 1013, 863, 855, 765, 758, 744, 705, 661, 649, 587, 572, 496, 457. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 8 Hz, 2H, H_a), 7.88 (d, J = 8 Hz, 2H, H_b), 7.61−7.59 (m, 2H, H_d), 7.41−7.38 (m, 3H, $H_{e/f}$), 5.66 (s, 2H, H_c), 4.13 (s, 3H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.32 (s, $C_{carbene}$), 148.81, 145.10, 133.24, 132.49, 130.73, 129.60, 129.29, 129.24, 124.44, 59.50, 38.36. HR-ESI-MS: m/z 1017.15 [Au(trz-c)-Cl-Au(trz-c)]$^+$ (calcd for $C_{32}H_{38}Au_2ClN_8O_8$ 1017.13), 785.20 [Au(trz-c)$_2$]$^+$ (calcd for $C_{32}H_{28}AuN_8O_4$ 785.19), 569.1 [Au(trz-c)(OS(CH$_3$)$_2$)]$^+$ (calcd for $C_{18}H_{20}AuClN_4O_3S$ 569.1), 549.0 [**7c** + Na]$^+$ (calcd for $C_{16}H_{14}AuClN_4NaO_2$ 549.04), 491.1 [**7c** − Cl^-]$^+$ (calcd for $C_{16}H_{14}AuN_4O_2$ 491.08). Anal. Calcd for $C_{16}H_{14}AuClN_4O_2$: C, 36.48; H, 2.68; N, 10.64. Found: C, 36.71; H, 2.63; N, 10.60.

Synthesis of Au(I) Complex 7d. To a solvent mixture of CH_2Cl_2 and CH_3CN (1/1, 10 mL) were added **6d** (138.0 mg, 0.392 mmol, 1.0 equiv), tetramethylammonium chloride (44.1 mg, 0.402 mmol, 1.0 equiv), and Ag_2O (49.5 mg, 0.214 mmol, 0.5 equiv). and the contents of the foil-covered reaction flask were stirred for 6 h. $Au(SMe_2)Cl$ (114 mg, 0.387 mmol, 1.0 equiv) was added, and the resulting mixture was stirred for 2 h. The reaction mixture was filtered through a Celite plug (CH_2Cl_2) and the solvent removed under reduced pressure to produce a colorless film. The colorless film was redissolved in CH_2Cl_2 (2 mL) and added dropwise into petroleum ether, resulting in a colorless precipitate. The precipitate was isolated by filtration to give a fine white powder (173 mg, 87%). Mp: 150 °C dec. IR: ν (cm^{-1}) 3032, 2950, 1601, 1583, 1527, 1492, 1455, 1420, 1343, 1321, 1229, 1181, 1150, 1079, 1029, 848, 773, 726, 713, 697, 670, 573, 468, 450. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57−7.55 (m, 2H, H_f), 7.44−7.22 (m, 8H, $H_{a/b/c/g/h}$), 5.64 (s, 2H, H_e), 4.18 (s, 2H, H_d), 3.84 (s, 3H, H_i). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.64 (s, $C_{carbene}$), 145.94, 134.99, 133.73, 129.32, 129.29, 129.17, 129.04, 128.55, 127.69, 58.94, 37.14, 31.24. HR-ESI-MS: m/z 955.19 [(Au(trz-d)-Cl-(Au(trz-d)]$^+$ (calcd for $C_{34}H_{34}Au_2ClN_6$ 955.19), 723.25 [Au(trz-d)$_2$]$^+$ (calcd for $C_{34}H_{34}AuN_6$ 723.25), 518.07 [**7d** + Na]$^+$ (calcd for $C_{17}H_{17}AuClN_3Na$ 518.07), 501.13 [Au(trz-d)(CH$_3$CN)]$^+$ (calcd for $C_{19}H_{20}AuN_4$ 501.14), 478.12 [Au(trz-d)(H$_2$O)]$^+$ (calcd for $C_{17}H_{19}AuN_3O$ 478.12), 460.11 [**7d** − Cl^-]$^+$ (calcd for $C_{17}H_{17}AuN_3$ 460.11), 264.15 [**6d** − BF_4^-]$^+$ (calcd for $C_{17}H_{18}N_3$ 264.15). Anal. Calcd for $C_{17}H_{17}AuClN_3$: C, 41.19; H, 3.46; N, 8.48. Found: C, 41.66; H, 3.62; N, 8.48.

Synthesis of Au(I) Complex 7e. To a solvent mixture of CH_2Cl_2 and CH_3CN (1/1, 10 mL) were added **6e** (203 mg, 0.627 mmol, 1.1 equiv), tetramethylammonium chloride (72 mg, 0.659 mmol, 1.1 equiv), and Ag_2O (73 mg, 0.321 mmol, 0.5 equiv), and the contents of the foil-covered reaction flask were stirred for 7 h. $Au(SMe_2)Cl$ (167 g, 0.570 mmol, 1.0 equiv) was added, and the resulting mixture was stirred for an additional 3 h. The mixture was filtered through a Celite plug (CH_2Cl_2), and the solvent was removed under reduced pressure to give a brown oil. The product was purified by silica chromatography (9/1 CH_2Cl_2/acetone), providing a colorless soild. This material was redissolved in CH_2Cl_2 (2 mL) and added dropwise into stirred petroleum ether, generating a white solid (267 mg, 89%), which was isolated by filtration. Mp: 227 °C dec. IR: ν (cm^{-1}) 3051, 2956, 1592, 1578, 1490, 1479, 1456, 1394, 1363, 1338, 1322, 1269, 1195, 1159, 1071, 1005, 920, 784, 769, 763, 699, 689, 673, 573, 510, 483. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09−8.06 (m, 2H, H_d), 7.71−7.69 (m, 2H, H_c), 7.56−7.53 (m, 6H, $H_{a/b/e/f}$), 4.20 (s, 3H, H_g). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.30 (s, $C_{carbene}$), 147.75, 139.12, 130.61, 130.58, 129.78, 129.65, 129.35, 126.28, 124.23, 38.17. HR-ESI-MS: m/z 957.1088 [2(**7e**) + Na]$^+$ (calcd for $C_{30}H_{26}Au_2Cl_2N_6Na$ 957.0826), 899.1209 [(Au(trz-e)-Cl-(Au(trz-e)]$^+$ (calcd for $C_{30}H_{26}Au_2ClN_6$ 899.1238), 667.1904 [Au(trz-e)$_2$]$^+$ (calcd for $C_{30}H_{26}AuN_6$ 667.1884), 490.0368 [**7e** + Na]$^+$ (calcd for $C_{15}H_{13}AuClN_3Na$ 490.0361), 270.0800 [(trz-e) + Cl]$^+$ (calcd for $C_{15}H_{13}ClN_3$ 270.0798). Anal. Calcd for $C_{15}H_{13}AuClN_3$: C, 38.52; H, 2.80; N, 8.98. Found: C, 38.55; H, 2.83; N, 9.01.

Synthesis of Au(I) Complex 7f. To a solvent mixture of CH_2Cl_2 and CH_3CN (1/1, 10 mL) were added **6f** (184 mg, 0.452 mmol, 1.2 equiv), tetramethylammonium chloride (63 mg, 0.537 mmol, 1.4 equiv), and Ag_2O (53 mg, 0.229 mmol, 0.6 equiv), and the contents of the foil-covered reaction flask were stirred for 14 h. $Au(SMe_2)Cl$ (110 mg, 0.373 mmol, 1.0 equiv) was added, and the reaction mixture was stirred for an additional 2 h. The mixture was filtered through a Celite plug (CH_2Cl_2), and solvent was removed under reduced pressure to give a colorless oil. The product was purified by silica chromatography (gradient CH_2Cl_2 → 9/1 CH_2Cl_2/acetone), providing a colorless solid. This material was redissolved in CH_2Cl_2 (2 mL) and added dropwise into stirred petroleum ether, generating a white solid. Removal of the solvent mixture in vacuo provided a white microcrystalline solid (170 mg, 83%). Mp: >230 °C. IR: ν (cm^{-1}) 3022, 2952, 2922, 2856, 1757, 1726, 1612, 1534, 1458 (br), 1372, 1325, 1281, 1195, 1121, 1072, 1033, 845, 772, 738, 625, 610, 589, 564. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.00 (s, 4H, $H_{b,f}$), 3.88 (s, 3H, H_d), 2.36 (s, 3H, $H_{a/g}$), 2.35 (s, 3H, $H_{a/g}$), 2.10 (s, 6H, H_c), 2.07 (s, 6H, H_e). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.87 (s, $C_{carbene}$), 145.96, 141.03, 140.87, 137.99, 135.63, 134.21, 129.56, 129.21, 122.23, 36.82, 21.43, 21.38, 20.20, 17.54. HR-ESI-MS: m/z 1067.3024 [(Au(trz-f)-Cl-(Au(trz-f)]$^+$ (calcd for $C_{42}H_{50}Au_2ClN_6$ 1067.3116), 835.3698 [Au(trz-f)$_2$]$^+$ (calcd for $C_{42}H_{50}AuN_6$ 835.3762), 574.1270 [**7f** + Na]$^+$ (calcd for $C_{21}H_{25}AuClN_3Na$ 574.1300). Anal. Calcd for $C_{21}H_{25}AuClN_3$: C, 45.70; H, 4.57; N, 7.61. Found: C, 45.99; H, 4.61; N, 7.65.

Synthesis of Pd(II) Complex 8b. Bis(μ-bromo)bis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromopalladium(II) (94 mg, 0.100 mmol, 1.0 equiv) and tetra-*n*-butylammonium bromide (TBAB) (66 mg, 0.205 mmol, 2.0 equiv) were heated at reflux in $CHCl_3$ (5 mL) for 3 h. The solvent was removed in vacuo, the orange powder was redissolved in CH_2Cl_2 (15 mL), and then Ag_2O (28 mg, 0.121 mmol, 1.2 equiv) and **6b** (78 mg, 0.212 mmol, 2.1 equiv) were added. The resulting reaction mixture was stirred at room temperature for 24 h and then filtered through Celite. The filtrate was washed with water (5 × 50 mL) and dried ($MgSO_4$) and then the solvent removed in vacuo.

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The crude mixture was purified via column chromatography (silica, CH_2Cl_2), to give the product as a light yellow solid (104 mg, 69%). Mp: >230 °C. IR: ν (cm^{-1}) 3035, 2976, 2935, 2838, 1610, 1574, 1474, 1438, 1420, 1395, 1386, 1313, 1292, 1255, 1178, 1143, 1093, 1076, 1022, 888, 827, 806, 749, 694, 653, 614, 594, 549, 518. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, J = 10 Hz, 2H, H_i), 7.76 (d, J = 10 Hz, 2H, H_k), 7.50 (m, 2H, H_b), 7.43 (t, J = 10 Hz, 2H, H_l), 7.38 (t, J = 5 Hz, 1H, H_m), 7.15 (m, 2H, H_a), 7.09 (d, J = 10 Hz, 2H, H_h), 6.09 (s, 2H, H_n), 6.06 (spt, J = 7 Hz, 1H, H_d), 6.05 (spt, J = 7 Hz, 1H, H_f), 3.96 (s, 3H, H_j), 3.91 (s, 3H, H_g), 1.71 (d, J = 7 Hz, 6H, H_e), 1.64 (d, J = 7 Hz, 6H, H_c). ^{13}C NMR (125 MHz, $CDCl_3$): δ 180.44 (s, $C_{carbene(bimy)}$), 160.62, 159.00 (s, $C_{carbene(trz)}$), 145.17, 134.80, 133.76, 132.25, 129.44, 128.89, 128.60, 121.84, 121.83, 120.64, 113.94, 112.56, 58.48, 55.55, 53.79, 53.59, 36.99, 21.20, 21.06. HR-ESI-MS: m/z 770.0095 [**8b** + Na]$^+$ (calcd for $C_{30}H_{35}Br_2N_5NaOPd$ 770.0128), 726.0625 [PdBr(Cl)-(iPr_2-bimy)(trz-b) + Na]$^+$ (calcd for $C_{30}H_{35}BrClN_5NaOPd$ 726.0623), 668.1040 [**8b**-Br$^-$]$^+$ (calcd for $C_{30}H_{35}BrN_5OPd$ 668.1038), 624.1547 [PdCl(iPr_2-bimy)(trz-b)]$^+$ (calcd for $C_{30}H_{35}ClN_5OPd$ 624.1563), 586.1810 [Pd(iPr_2-bimy)(trz-b) − H]$^+$ (calcd for $C_{30}H_{34}N_5OPd$ 586.1804), 358.0563 [(trz-b) + Br]$^+$ (calcd for $C_{17}H_{17}BrN_3O$ 358.0555). Anal. Calcd for $C_{30}H_{35}Br_2N_5OPd$: C, 48.18; H, 4.72; N, 9.36. Found: C, 48.39; H, 4.70; N, 9.38.

Synthesis of Pd(II) Complex 8c. Bis(μ-bromo)bis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromopalladium(II) (94 mg, 0.100 mmol, 1.0 equiv) and TBAB (66 mg, 0.204 mmol, 2.0 equiv) were heated at reflux in $CHCl_3$ (5 mL) for 4 h. The solvent was removed in vacuo, the orange powder was redissolved in CH_2Cl_2 (15 mL), and then Ag_2O (28 mg, 0.121 mmol, 1.2 equiv) and **6c** (98 mg, 0.202 mmol, 2.0 equiv) were added. The reaction mixture was stirred at room temperature for 36 h and then filtered through Celite. The filtrate was washed with H_2O (5 × 50 mL) and the aqueous layer discarded. The organic layer was removed in vacuo, and the resulting yellow residue was purified via column chromatography (silica, CH_2Cl_2), to give the product as a yellow solid (104 mg, 68%). Mp: >230 °C. IR: ν (cm^{-1}) 3093, 3063, 3029, 2971, 2937, 2879, 1601, 1518, 1456, 1420, 1398, 1386, 1358, 1343, 1312, 1142, 1092, 1078, 1023, 865, 856, 757, 704, 647, 598, 547, 496, 458, 424. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.43 (d, J = 10 Hz, 2H, H_g), 8.28 (d, J = 10 Hz, 2H, H_h), 7.74 (d, J = 8 Hz, 2H, H_j), 7.51 (dd, J = 7, 3 Hz, 2H, H_b), 7.45 (t, J = 8 Hz, 2H, H_k), 7.40 (m, J = 8 Hz, 1H, H_l), 7.17 (dd, J = 7, 3 Hz, 2H, H_a), 6.15 (s, 2H, H_m), 5.97 (m, J = 7 Hz, 2H, $H_{d/f}$), 4.06 (s, 3H, H_i), 1.70 (d, J = 7 Hz, 6H, H_c), 1.65 (d, J = 7 Hz, 6H, H_e). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.95 (s, $C_{carbene(bimy)}$), 161.91 (s, $C_{carbene(trz)}$), 148.50, 143.44, 134.89, 134.36, 133.67, 131.81, 129.30, 129.00, 128.83, 123.65, 122.05, 112.66, 58.72, 53.92, 53.75, 37.53, 21.11, 21.02. HR-ESI-MS: m/z 1548.9823 [2(**8c**) + Na]$^+$ (calcd for $C_{58}H_{64}Br_4N_{12}NaO_4Pd_2$ 1548.9854), 1503.0305 [**8c**+PdBr(Cl)(iPr_2-bimy)(trz-c) + Na]$^+$ (calcd for $C_{58}H_{64}Br_3ClN_{12}NaO_4Pd_2$ 1503.0366), 784.9826 [**8c** + Na]$^+$ (calcd for $C_{29}H_{32}Br_2N_6NaO_2Pd$ 784.9873), 741.0341 [PdBr(Cl)(iPr_2-bimy)(trz-c) + Na]$^+$ (calcd for $C_{29}H_{32}BrClN_6NaO_2Pd$ 741.0368), 683.0756 [**8c** − Br$^-$]$^+$ (calcd for $C_{29}H_{32}BrN_6O_2Pd$ 683.0783), 373.0254 [(trz-c) + Br]$^+$ (calcd for $C_{16}H_{14}BrN_4O_4$ 373.0295), 295.1178 [**6c** − BF_4^-]$^+$ (calcd for $C_{16}H_{15}N_4O_2$ 295.1190). Anal. Calcd for $C_{29}H_{33}Br_2N_6O_2Pd$: C, 45.66; H, 4.23; N, 11.02. Found: C, 45.96; H, 4.26; N, 11.02.

Synthesis of Pd(II) Complex 8d. Bis(μ-bromo)bis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromopalladium(II) (93 mg, 0.099 mmol, 1.0 equiv) and TBAB (67 mg, 0.208 mmol, 2.0 equiv) were heated at reflux in $CHCl_3$ (5 mL) for 4 h. The solvent was removed in vacuo, the orange powder was redissolved in CH_2Cl_2 (15 mL), and then Ag_2O (30 mg, 0.129 mmol, 1.3 equiv) and **6d** (98 mg, 0.198 mmol, 2.0 equiv) were added. The reaction mixture was stirred at room temperature for 24 h and then filtered through Celite. The filtrate was removed in vacuo and the crude mixture purified via column chromatography (silica, CH_2Cl_2), to give the product as a light yellow solid (101 mg, 70%). Mp: >230 °C. IR: ν (cm^{-1}) 3088, 2976, 2935, 2873, 1602, 1584, 1495, 1474, 1454, 1420, 1396, 1387, 1312, 1231, 1175, 1141, 1093, 1074, 848, 807, 750, 736, 729, 713 695, 548, 456. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 (d, J = 7 Hz, 2H, H_l), 7.57 (d, J = 8 Hz, 2H, H_h), 7.50 (m, 2H, H_b), 7.43 (t, J = 7 Hz, 2H, H_m), 7.37 (t, J = 8 Hz, 3H, $H_{i,j}$), 7.28 (t, J = 8 Hz, 1H, H_n), 7.16 (m, 2H, H_a), 6.13 (s, 2H, H_o), 6.05 (spt, J = 7 Hz, 1H, H_d), 5.93 (spt, J = 7 Hz, 1H, H_f), 4.62 (s, 2H, H_g), 3.78 (s, 3H, H_k), 1.66 (d, J = 7 Hz, 6H, H_c), 1.64 (d, J = 7 Hz, 6H, H_e). ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.70 (s, $C_{carbene(bimy)}$), 158.99 (s, $C_{carbene(trz)}$), 144.23, 136.83, 135.34, 133.84, 133.76, 129.04, 129.02, 128.85, 128.65, 128.36, 127.07, 121.86, 112.59, 58.07, 53.74, 36.31, 31.85, 21.05. HR-ESI-MS: m/z 754.0122 [**8d** + Na]$^+$ (calcd for $C_{30}H_{35}Br_2N_5NaPd$ 754.0179), 710.0593 [PdBr(Cl)-(iPr_2-bimy)(trz-d) + Na]$^+$ (calcd for $C_{30}H_{35}BrClN_5NaPd$ 710.0674), 652.1047 [**8d** − Br$^-$]$^+$ (calcd for $C_{30}H_{35}BrN_5Pd$ 652.1088), 344.0554 [(trz-d) + Br]$^+$ (calcd for $C_{17}H_{17}BrN_3$ 344.0580). Anal. Calcd for $C_{30}H_{35}Br_2N_5Pd$: C, 49.23; H, 4.82; N, 9.57. Found: C, 49.48; H, 5.03; N, 9.52.

Synthesis of Pd(II) Complex 8e. Bis(μ-bromo)bis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromopalladium(II) (94 mg, 0.100 mmol, 1.0 equiv) and TBAB (68 mg, 0.211 mmol, 2.1 equiv) were heated at reflux in $CHCl_3$ (5 mL) for 3 h. The solvent was removed in vacuo, the orange powder was redissolved in CH_2Cl_2 (15 mL), and then Ag_2O (28 mg, 0.121 mmol, 1.2 equiv) and **6e** (68 mg, 0.210 mmol, 2.1 equiv) were added. The reaction mixture was stirred at room temperature for 24 h and then filtered through Celite. The filtrate was washed with H_2O (4 × 50 mL) and the aqueous layer discarded. The organic layer was removed in vacuo, and the yellow residue was purified via column chromatography (silica, 9/1 CH_2Cl_2/acetone), to give the product as a yellow solid (91 mg, 64%). Mp: >230 °C. IR: ν (cm^{-1}) 3058, 3006, 2979, 2935, 2880, 1594, 1497, 1474, 1423, 1401, 1388, 1369, 1315, 1261, 1175, 1143, 1093, 1074, 1020, 924, 778, 765, 749, 703, 692, 681, 604, 547, 522, 484. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.49 (d, J = 10 Hz, 2H, H_k), 8.14 (d, J = 10 Hz, 2H, H_i), 7.62 (m, 6H, $H_{l/m/h/g}$), 7.47 (m, 2H, H_b), 7.13 (dd, J = 8 Hz, 2H, H_a), 5.87 (spt, J = 7 Hz, 1H, $H_{d/f}$), 5.86 (spt, J = 7 Hz, 1H, $H_{d/f}$), 4.15 (s, 3H, H_j), 1.62 (d, J = 7 Hz, 6H, $H_{c/e}$), 1.58 (d, J = 7 Hz, 6H, $H_{c/e}$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 179.87 (s, $C_{carbene(bimy)}$), 160.08 (s, $C_{carbene(trz)}$), 145.25, 140.11, 133.80, 133.67, 131.00, 129.82, 129.75, 128.88, 128.64, 128.20, 125.75, 121.82, 112.49 53.68, 53.58, 37.35, 21.03, 21.02. HR-ESI-MS: m/z 1430.9643 [2(**8e**) + Na]$^+$ (calcd for $C_{56}H_{62}Br_4N_{10}NaPd_2$ 1430.9823), 1327.0628 [**8e**+(**8e**-Br$^-$)]$^+$ (calcd for $C_{56}H_{62}Br_3N_{10}Pd$ 1327.0762), 725.9799 [**8e** + Na]$^+$ (calcd for $C_{28}H_{32}Br_2N_5NaPd$ 725.9858), 624.0727 [**8e** − Br$^-$]$^+$ (calcd for $C_{28}H_{31}BrN_5Pd$ 624.0777), 578.1231 [PdCl(iPr_2-bimy)(trz-e)]$^+$ (calcd for $C_{28}H_{31}ClN_5Pd$ 578.1303). Anal. Calcd for $C_{28}H_{31}Br_2N_5Pd$: C, 47.78; H, 4.44; N, 9.95. Found: C, 47.74; H, 4.37; N, 9.96.

Synthesis of Pd(II) Complex 8f. Bis(μ-bromo)bis(1,3-diisopropylbenzimidazolin-2-ylidene)dibromopalladium(II) (93 mg, 0.099 mmol, 1.0 equiv) and TBAB (68 mg, 0.211 mmol, 2.1 equiv) were heated at reflux in $CHCl_3$ (5 mL) for 3 h. The solvent was removed in vacuo, the orange powder was redissolved in CH_2Cl_2 (15 mL), and then Ag_2O (36 mg, 0.155 mmol, 1.6 equiv) and **6f** (89 mg, 0.219 mmol, 2.2 equiv) were added. The reaction mixture was stirred at room temperature for 18 h. After this time the reaction mixture was filtered through Celite, the solvent of the filtrate was removed in vacuo, and the crude mixture was purified via column chromatography (silica, 9/1 CH_2Cl_2/acetone) to give the product as a yellow solid (112 mg, 72%). Mp: >230 °C. IR: ν (cm^{-1}) 3056, 2975, 2919, 1612, 1475, 1422, 1401, 1369, 1315, 1271, 1183, 1142, 1093, 1062, 1022, 846, 740, 564. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (dd, J = 6, 4 Hz, 2H, H_b), 7.07 (m, 6H, $H_{a/h/l}$), 5.56 (spt, J = 6 Hz, 2H, $H_{d/f}$), 3.87 (s, 3H, H_j), 2.43 (s, 3H, $H_{g/m}$), 2.41 (s, 3H, $H_{g/m}$), 2.37 (s, 6H, $H_{i/k}$), 2.36 (s, 6H, $H_{i/k}$), 1.50 (d, J = 7 Hz, 12H, $H_{c/e}$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.99 (s, $C_{carbene(bimy)}$), 162.32 (s, $C_{carbene(trz)}$), 144.94, 139.79, 139.62, 136.37, 136.10, 133.89, 128.91, 128.51, 124.18, 121.56, 112.08, 53.23, 36.04, 21.60, 21.47, 21.37, 21.02, 19.56. HR-ESI-MS: m/z 1599.1626 [2(**8f**) + Na]$^+$ (calcd for $C_{68}H_{86}Br_4N_{10}NaPd_2$ 1559.1722), 1553.2211 [**8f** + PdBr(Cl)(iPr_2-bimy)(trz-**f**) + Na]$^+$ (calcd for $C_{68}H_{86}Br_3ClN_{10}NaPd_2$ 1553.2233), 810.0739 [**8f** + Na]$^+$ (calcd for $C_{34}H_{43}Br_2N_5NaPd$ 810.0806), 766.1233 [PdBr(Cl)(iPr_2-bimy)(trz-f) + Na]$^+$ (calcd for $C_{34}H_{43}BrClN_5NaPd$ 766.1300), 708.1665 [**8f** − Br$^-$]$^+$ (calcd for $C_{34}H_{43}BrN_5NaPd$ 708.1715), 320.2082 [**6f** − BF_4^-]$^+$ (calcd for $C_{21}H_{26}N_3$ 320.2121). Anal. Calcd for $C_{34}H_{43}Br_2N_5Pd$: C, 51.83; H, 5.50; N, 8.89. Found: C, 51.81; H, 5.54; N, 8.87.

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Representative Procedure for the Skeletal Rearrangement of 9. Au(trz)Cl (0.0063 mmol, 5 mol %) was added to a solution of **9**[30a] (30 mg, 0.126 mmol) in CH_2Cl_2 (1 mL). In a separate vial, silver hexafluoroantimonate (2.2 mg, 0.0063 mmol, 5 mol %) was dissolved in CH_2Cl_2 (0.1 mL), and then this solution was transferred to **9** and washed in with CH_2Cl_2 (0.14 mL). The reaction mixture was stirred for 1 min at 23 °C, followed by immediate purification by flash column chromatography (silica, gradient neat petroleum ether → 7/1 petroleum ether/diethyl ether). Product **10** was obtained as a colorless oil. Spectroscopic analyses were in agreement with those previously reported in the literature.[30] IR: ν (cm^{-1}) 2954 w, 2917 w, 2853 w (C−H), 1733 s (C═O), 1653 w (C═C), 1249 s (C−O−C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.73 (br s, 1H, C═C*H*), 5.38 (br s, 1H, C═C*H*), 3.73 (s, 6H, CO_2CH_3), 3.19 (br s, 2H, CH_2), 3.04 (br s, 2H, CH_2), 1.82 (s, 3H, CH_3), 1.78 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.8 (C), 138.9 (C), 135.8 (C), 124.6 (CH), 120.8 (CH), 59.5 (C), 53.0 (CH_3), 43.4 (CH_2), 40.4 (CH_2), 27.4 (CH_3), 20.0 (CH_3).

Representative Procedure for Allylic Etherification Reaction. The gold(I) catalyst (0.0058 mmol, 5 mol %) was added to a solution of allylic alcohol **12**[34a] (15 mg, 0.117 mmol) and 4-phenylbutanol (**13**; 19.6 μL, 19.3 mg, 0.129 mmol, 1.1 equiv) in CH_2Cl_2 (0.1 mL). In a separate vial, silver hexafluoroantimonate (2.0 mg, 0.0058 mmol, 5 mol %) was dissolved in CH_2Cl_2 (0.1 mL) and then transferred to the reaction mixture and washed in with CH_2Cl_2 (0.1 mL). The reaction was stirred for 18 h at 25 °C. The crude mixture was filtered through a silica plug with diethyl ether and concentrated under reduced pressure. The product **14** was obtained as a colorless oil after purification by flash column chromatography (silica, gradient neat hexane → 50/1 hexane/diethyl ether). Spectroscopic analyses were in agreement with those previously reported in the literature.[34a] IR: ν (cm^{-1}) 3027 w, 2954 m, 2937 m, 2862 m (C−H), 1655 w (C═C), 1604 w, 1496 m, 1453 m (aromatic C═C), 1107 s (C−O−C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.15 (m, 5H, Ar−H), 5.39 (tq, J = 6.2, 1.2 Hz, 1H, OCH_2CH), 4.00 (d, J = 6.2 Hz, 2H, OCH_2CH), 3.45 (t, J = 6.4 Hz, 2H, OCH_2CH_2), 2.65 (t, J = 7.4 Hz, 2H, CH_2CH_2Ph), 1.77 − 1.58 (m, 7H, alkyl CH_2 and $C(CH_3)$), 1.06 (s, 9H, $C(CH_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.0 (C), 142.6 (C), 128.6 (CH), 128.4 (CH), 125.8 (CH), 118.4 (CH), 70.4 (CH_2), 68.3 (CH_2), 36.4 (C), 35.9 (CH_2), 29.6 (CH_2), 29.0 (CH_3), 28.3 (CH_2), 13.2 (CH_3). HRMS (EI): m/z calcd for $C_{18}H_{28}O$ $[M]^+$ 260.2135, found 260.2136.

X-ray Collection and Refinement. X-ray data were recorded using a Bruker Kappa X8 APEX II CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Semiempirical absorption corrections (SCALE) were applied. The structures were solved by SHELXS-97.[38] Full-matrix least-squares refinement on F^2 was carried out using SHELXL-97 via the X-Seed graphical interface.[39] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions and were refined as riding atoms with individual (or group, if appropriate) isotropic displacement parameters.

Special Conditions/Variations. **7b**: the benzyl group (C9−C15) appeared to be rotationally disordered about the C11/C14 phenyl ring axis and was modeled over three positions, refining to 0.5:0.25:0.25 occupancies. The disordered fragment was refined with the use of SAME, FLAT, EADP, and ISOR restraints/constraints. The largest residual electron density peaks are ca. 1 Å from the gold atom.

8d: the whole dibenzylmethyltriazolylidene ligand (C1−C17, N1−N3) appeared to be rotationally disordered about the Pd1−C1 bond (by ca. 180° for the triazolyl ring). The triazolylidene ligand and both bromide ligands were modeled over two positions, refining to 0.75:0.25 occupancies. The disordered triazolylidene ligand was refined with the use of SAME restraints across the two orientations, and a FLAT restraint and EADP constraints were applied to each ring.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIFs giving spectroscopic, crystallographic and molecular modeling data for **6a−f**, **7a−f** and **8b−f**. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic data are also available from the Cambridge Crystallographic Database as file nos. CCDC 932209−932216.

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Notes

The authors declare no competing financial interest.

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