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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

James R. Wright,†,§ Paul C. Young,†,§ Nigel T. Lucas,† Ai-Lan Lee,*‡ and James D. Crowley*†

1Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand
2Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, U.K.

Supporting Information

INTRODUCTION

In the past two decades N-heterocyclic carbenes (NHCs) have become the ligands of choice for new catalyst development. Initially, Arduengo-type imidazol-2-ylidene complexes (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), cyclic alkylaminocarbenes (CAAC, E), pyrid-2-ylidenes (F), pyrid-4-ylidenes (G), pyrazol-4-ylidenes (H), 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. These NHCs have been termed abnormal NHCs (aNHC)/mesionic carbenes (MICs) because no sensible uncharged resonance structures can be generated for these systems. They have attracted considerable attention since their discovery in 2008 because the 1,4-disubstituted 1,2,3-triazole units, from which the aNHC/MICs are derived, are readily synthesized and functionalized using the modular and functional group tolerant copper(1)-catalyzed cycloaddition of azides and alkynes (CuAAC) “click” reaction. Copper, palladium, ruthenium, and iridium 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. 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. 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, we recently reported the synthesis of the Au(trz)Cl complex 7a (Scheme 1) and showed that it was catalytically active. 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-ylidine’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-
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,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 ([Me3O]BF4) (Scheme S1, Supporting Information.).11d,18,20 The infrared spectra (IR) of 6a−f confirm the presence of both the triazole unit (νC−H 3150−2965 cm−1) and the BF4− anions (νB−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 [(6a−f)−(BF4−)]+ and [2(6a−f)−(BF4−)]+ 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 13C 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 CH2Cl2/CH3CN and treated with Ag2O in the presence of Me4NCl to generate the silver(I) 1,2,3-triazolylidene complexes in situ. Addition of Au(SMe2)Cl to the in situ generated silver(I) 1,2,3-triazolylidene 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 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-[PdBr2(iPr2-bimy)(trz)] (where iPr2-bimy = 1,3-diisopropylbenzimidazolin-2-ylidene) in good to excellent yields (64−86%). These gold(I) and palladium(II) compounds were
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(ipPr-bimy)(trz)]⁺, [PdCl(ipPr-bimy)(trz)]⁺, and [PdBr$_2$(ipPr-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.$^7$\textsuperscript{a,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 and a chloride ligand in the expected linear fashion (C–H–O = 2.690(3) Å, C–O = 3.592(6) Å). Additionally, π–π 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$^{28}$ 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 complexes 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).
3) with those previously reported. 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 (Table 1) and consistent with what has been observed previously for 1,2,3-triazolylidienes. The bromide ligands of the complexes angle toward the benzimidazolylidene carbene carbon, due to back-donation from the bromide ligand to the empty p orbital of the carbon (Cpally − Br = 3.048(3)–3.147(5) Å; C−Br(VDW) = 3.55 Å). Additionally, this is supported by the shorter C21−Pd1 bond length in comparison to the triazolylidylic C1−Pd1 bond (Table 2). The “unusual” interaction of the tertiary isopropyl hydrogens and the palladium center, previously discussed by Huynh, is also present in the structures (Pd···H−C = 2.6592(2)–2.7738(4) Å).

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 substituted and the N-bound benzyl group of an adjacent molecule (C−H···π distance can be a set of palladium complexes.

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) |

Figure 3. ORTEP 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.

Ligand Donor Properties. The mild CuAAC “click” methodology used to generate the 1,3,4-trisubstituted 1,2,3-triazolylidene ligands potentially provides a facile way to tune both steric and electronic properties of the resulting carbene complexes. The M−Cu complexes 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 (wингtip) substitution of the compounds 7a−f and 8a−f. The Au−Cu bond lengths of the gold(I) complexes 7b (aryl-OMe) < 7a (aryl-H) < 7c (aryl-NO2) follow the expected trend with the more electron rich methoxy-substituted complex 7b displaying a shorter Au−Cu bond than the parent complex 7a. Similarly, the electron-poor nitro-substituted complex 7c has a longer Au−Cu bond than the parent complex 7a. However, the observed differences are a similar magnitude to the experimental uncertainty (Table 1). The correlation breaks down with complexes 7df, where the observed Au−Cu bond lengths are longer (7d) and shorter (7f) than would be predicted on the basis of inductive arguments. Furthermore, the Pd−Cu 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−Cu 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 13C NMR spectra of palladium complexes 8a−f were used to provide insight into
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 $\sigma$-donor strength of the ligands trans to the benzimidazol-2-ylidene.\textsuperscript{21,28} They have found that there is a direct relationship between $\sigma$-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.\textsuperscript{21,28} Additionally, this system has previously been used to show that the mesoionic trz ligands are stronger donors than imidazol-2-ylidene.\textsuperscript{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,\textsuperscript{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 ($\delta$ 180.44 ppm), relative to the ligand in 8a, suggesting that the 4-MeOC$_6$H$_5$-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 ($\delta$ 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 $\sigma$-donor strength ($\delta$ 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 ($\delta$ 179.70 ppm) and the dimesityl-substituted complex 8f ($\delta$ 178.99 ppm) was unexpected. The data suggest that these ligands are weaker $\sigma$ 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 $\sigma$ 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 $\sigma$-donor properties. $^1$H NMR spectroscopic and X-ray crystallographic data provide some support for this theory. The $^1$H 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)\textdegree). 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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**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,\textsuperscript{29} not 77.7 ppm as reported in the original Huynh papers.\textsuperscript{21,27}
9 was subjected to skeletal rearrangement catalyzed by various Au(trz)Cl precatalysts—a typical test reaction for catalytic activity of new gold complexes (Table 3). Our initial 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 steric 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 rich (entry 5) as the electron-poor Bn,Ph-substituted Au(trz)Cl 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. 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 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 aliphatic etherification using unactivated aliphatic alcohols and alcohol nucleophiles is possible using gold catalysis (e.g., Scheme 2). The original method requires excess (5 equiv) of the alcohol nucleophile (e.g., 13) for best results, using Au(PPh$_3$)NTf$_2$ as the catalyst. An excess of 13 is to ensure that the aliphatic 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 steric 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$_2$ 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.

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

| Entry | L:AuCl | Time (min) | Yield (%) |
|-------|--------|------------|-----------|
| 1     | 7a     | 15         | 1:2       | 42        |
| 2     | 7b     | 15         | 1:2       | 45        |
| 3     | 7d     | 15         | 1:2       | 50        |
| 4     | 7e     | 15         | 1:2       | 47        |
| 5     | 7a     | 1          | >20:1     | 92        |
| 6     | 7b     | 1          | 20:1      | 94        |
| 7     | 7c     | 1          | >20:1     | 95        |
| 8     | 7d     | 1          | 13:1      | 93        |
| 9     | 7e     | 1          | >20:1     | 72        |
| 10    | 7f     | 1          | >20:1     | 98        |
| 11    | 7f     | 1          | >20:1     | 93        |
| 12    | PPh$_3$AuCl | 25       | 10:1      | 91        |
| 13    | Bu$_3$NCMe | 5           | 10:1      | 98        |

“Determined by $^1$H NMR analysis. Isolated yields. Mixture of 10 and 11 as indicated. Ratio not reported. AgSbF$_6$ not added.

**Scheme 2. Example of Previous Conditions for Direct Allylic Etherification**

![Scheme 2](image)

75% yield of 14 (12:1 14:15 regioselectivity)
melting points were determined using a Mettler-Toledo FP62 apparatus and are uncorrected. 1H and 13C 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 (CDCl3, δ 7.26 ppm, 13C δ 77.16 ppm; CD2CN, δ 1.94, 13C 118.26 ppm).

Complete experimental details (i) are reported in the supporting information. Standard abbreviations indicating multiplicity used as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

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. CH3CN refers to acetonitrile, and CH2Cl2 is dichloromethane.

Au(trz)SbF6 (entry 9). Finally, the phosphine counterpart Au(PPh3)SbF6 provides poorer yields as well as selectivities for Generating Precatalysts and Palladium(II) Probe Complexes. The molecular structures of four of the gold(I) and four of the palladium(II) complexes were purchased from commercial sources and used without further purification.

In summary, the gold(I) complexes Au(trz)Cl (7a–f) in the allylic etherification 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.

Pleaseingly, 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).

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

| entry | L AuCl (5 mol%) | yield of 14, %b | E/Zc |
|-------|----------------|-----------------|-----|
| 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(PPh3)Cl     | 4:1 incomplete reactionb | 3:4:1|
| 8     | Au(Ir)Cl       | 2:5:1 incomplete reactionb | 3:2:5:1|
| 9     | Au(IMes)Cl     | >20:1 70        | 5:1 |
| 10    | Au(PPh3)Cl     | 17:1 61         | 4:1 |

* Determined by 1H NMR analysis. b Isolated yields of 14. c Using 2,3,5,6-tetrachloronitrobenzene as internal standard. No AgSbF6 added.

Au(trz)SbF6 (entry 9). Finally, the phosphine counterpart Au(PPh3)SbF6 provides poorer yields as well as selectivities (entry 10) than the Au(trz)SbF6 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 1H and 13C 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 electronic and steric alteration of the side-arm substituents (wingtip groups) has been assessed using the palladium(II) probe complexes.

In the allylic etherification 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. Pleaseingly, 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).
Synthesis of Au(I) Complex 7b. To a solvent mixture of CH2Cl2 and CHCN (1/1, 10 mL) were added 6b (0.142 mg, 0.387 mmol, 1.0 equiv), tetramethyloxonium chloride (43 mg, 0.392 mmol, 1.0 equiv), and Ag2O (45 mg, 0.194 mmol, 0.5 equiv), and the contents of the foil-covered reaction flask were stirred for 5 h. Au(SMe2)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 (CH2Cl2) and the solvent removed under reduced pressure to give a brown oil. The product was purified by vacuum filtration through a concentrated CH2Cl2 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, 2906, 2936, 2907, 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. ¹H NMR (400 MHz, CDCl3): δ 7.63 – 7.61 (m, 2H, Hf, He), 7.56 (s, 2H, Hg). ¹³C NMR (100 MHz, CDCl3): 161.18 (C phenyl), 157.54, 147.16, 137.39, 131.09, 129.28, 129.21, 129.12, 118.23, 114.73, 59.13, 55.38, 37.86. HR-ESI-MS: m/z 987.1759 [Au(trz-d)-Cl-Au(trz-d)]⁺ (calcd for C61H55Au2ClN6O2) 987.1763 755.2396 [Au(trz-b)]⁺ (calcd for C59H51Au2N6O2).

Synthesis of Au(I) Complex 7c. A solution of CH2Cl2 and CHCN (1/1, 10 mL) were added 6c (217 mg, 0.568 mmol, 1.2 equiv), tetramethylammonium chloride (63 mg, 0.573 mmol, 1.2 equiv), and Ag2O (73 mg, 0.321 mmol, 0.5 equiv), and the contents of the foil-covered reaction flask were stirred for 7 h. Au(SMe2)Cl (0.255 g, 0.707 mmol, 1.0 equiv) was added, and the reaction mixture was stirred for 3 h. The mixture was filtered through a Celite plug (CH2Cl2), and the solvent was removed under reduced pressure to give a yellow oil, which was purified by column chromatography (gradient CH2Cl2). A concentrated CH2Cl2 solution of the product was crystallized by vacuum evaporation of diethyl ether to produce bright yellow crystals (172 mg, 72%). Mp: 170 °C dec. IR: ν (cm⁻¹) 3084, 2925, 2888, 1601, 1520, 1516, 1498, 1479, 1544, 1435, 1341 (br), 1287, 1165, 1106, 1091, 1076, 1044, 1013, 863, 855, 765, 758, 744, 705, 661, 649, 587, 572, 496, 457. ¹H NMR (400 MHz, CDCl3): δ 8.33 (d, J = 8 Hz, 2H, Hf, He), 7.78 (d, J = 8 Hz, 2H, Hg). ¹³C NMR (125 MHz, CDCl3): δ 137.24, 134.37, 130.17, 114.03, 126.90, 122.24, 121.44, 59.50, 38.36. HR-ESI-MS: m/z 1017.15 [Au(trz-d)-Cl-Au(trz-d)]⁺ (calcd for C61H55Au2ClN6O2) 1017.13, 785.20 [Au(trz-c)]⁺ (calcd for C61H55Au2ClN6O2). ¹H NMR (500 MHz, CDCl3): 7.78 (m, 6H, Ha/b/e/f), 4.13 (s, 3H, Hg).

Synthesis of Au(I) Complex 7d. To a solvent mixture of CH2Cl2 and CHCN (1/1, 10 mL) were added 6d (184 mg, 0.452 mmol, 1.2 equiv), tetramethyloxonium chloride (44.1 mg, 0.402 mmol, 1.0 equiv), and Ag2O (53 mg, 0.229 mmol, 0.6 equiv), and the contents of the foil-covered reaction flask were stirred for 14 h. Au(SMe2)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 (CH2Cl2), and solvent was removed under reduced pressure to give a colorless oil. The product was purified by silica chromatography (gradient CH2Cl2 → 9/1 CH2Cl2/acetone), providing a colorless solid. This material was redissolved in CH2Cl2 (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: v (cm⁻¹) 3051, 2956, 1592, 1578, 1490, 1479, 1456, 1394, 1333, 1322, 1269, 1195, 1159, 1071, 1005, 780, 763, 699, 689, 673, 573, 510, 483. ¹H NMR (500 MHz, CDCl3): 6.89 – 8.06 (m, 2H, Hf, He), 7.71 – 7.69 (m, 2H, Hg). ¹³C NMR (125 MHz, CDCl3): δ 167.30 (C phenyl), 147.75, 139.12, 130.61, 130.48, 129.78, 129.65, 129.35, 128.63, 124.23, 38.17. HR-ESI-MS: m/z 957.1088 [2(7e + Na)⁺] (calcd for C46H30Au2ClNa2 957.1082, 899.1209 [Au(trz-e)-Cl-Au(trz-e)]⁺ (calcd for C46H30Au2ClNa2). Removal of the solvent mixture in vacuo provided a white microcrystalline solid (170 mg, 83%). Mp: > 230 °C. IR: v (cm⁻¹) 3022, 2952, 2922, 2856, 1757, 1726, 1612, 1534, 1458 (br), 1372, 1325, 1313, 1195, 1121, 1073, 1033, 845, 772, 738, 625, 589, 564. ¹H NMR (500 MHz, CDCl3): 6.00 – 7.00 (8H, 2H, Hf, He), 3.88 (3H, Hg). ¹³C NMR (125 MHz, CDCl3): δ 161.87 (C phenyl), 149.65, 141.03, 140.87, 139.72, 134.21, 133.24, 134.04, 132.72, 129.19, 126.94, 59.50, 38.36.

Synthesis of Pd(II) Complex 8a. Bis(μ-bromo)bis(1,3-dioisopropylbenzimidazolin-2-ylidene)dibromopalladium(II) (94 mg, 0.101 mmol, 1.0 equiv) and tetrabutylammonium bromide (TBAB) (66 mg, 0.205 mmol, 2.0 equiv) were heated at reflux in CHCl3 (5 mL) for 3 h. The solvent was removed in vacuo, the orange powder was redissolved in CH2Cl2 (15 mL) and then Ag2O (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 (MgSO4) and then the solvent removed in vacuo.
The crude mixture was purified via column chromatography (silica, CH₂Cl₂), to give the product as a light yellow solid (104 mg, 69%). Mp: >230 °C. IR: ν (cm⁻¹): 3035, 2975, 2935, 2838, 1610, 1574, 1474, 1438, 1420, 1395, 1386, 1313, 1295, 1255, 1178, 1143, 1093, 1076, 1022, 888, 827, 806, 749, 694, 653, 614, 594, 549, 518. ¹H NMR (500 MHz, CDCl₃): δ 7.93 (d, J = 10 Hz, 2H, H₂), 7.76 (d, J = 10 Hz, 2H, H₂), 7.50 (m, 2H, H₂), 7.15 (m, 2H, H₂), 7.09 (d, J = 10 Hz, 2H, H₂), 6.09 (s, 2H, H₂), 6.06 (spt, J = 7 Hz, 1H, H₁), 6.05 (spt, J = 7 Hz, 1H, H₁), 3.96 (s, 3H, H₃), 3.91 (s, 3H, H₃), 1.71 (t, J = 7 Hz, 6H, H₄), 1.64 (d, J = 7 Hz, 6H, H₄). ¹³C NMR (125 MHz, CDCl₃): δ 180.44 (s, C(carbene(bimy))), 160.62, 159.00 (s, C(benzene)), 145.17, 134.80, 137.36, 132.25, 124.49, 128.89, 126.60, 121.84, 121.83, 126.64, 119.24, 115.58, 54.58, 55.55, 53.79, 53.59, 36.99, 21.10, 20.16. HR-ESI-MS: m/z 770.0095 [8b + Na]⁺ (calcd for C₂₉H₃₄Br₃N₆O₂Pd).

Synthesis of Pd(II) Complex 8a. Bis(μ-bromo)(1,3-disopropylbenzimidazol-2-ylidene)diacrolein(dipalladium(II) (94 mg, 0.101 mmol, 1.0 equiv) and TBAB (66 mg, 0.204 mmol, 2.0 equiv) were heated at reflux in CHCl₃ (5 mL) for 4 h. The solvent was removed via column chromatography (silica, CH₂Cl₂), to give the product as a light yellow solid (104 mg, 69%). Mp: >230 °C. IR: ν (cm⁻¹): 3035, 2975, 2935, 2838, 1610, 1574, 1474, 1438, 1420, 1395, 1386, 1313, 1295, 1255, 1178, 1143, 1093, 1076, 1022, 888, 827, 806, 749, 694, 653, 614, 594, 549, 518. ¹H NMR (500 MHz, CDCl₃): δ 7.93 (d, J = 10 Hz, 2H, H₂), 7.76 (d, J = 10 Hz, 2H, H₂), 7.50 (m, 2H, H₂), 7.15 (m, 2H, H₂), 7.09 (d, J = 10 Hz, 2H, H₂), 6.09 (s, 2H, H₂), 6.06 (spt, J = 7 Hz, 1H, H₁), 6.05 (spt, J = 7 Hz, 1H, H₁), 3.96 (s, 3H, H₃), 3.91 (s, 3H, H₃), 1.71 (t, J = 7 Hz, 6H, H₄), 1.64 (d, J = 7 Hz, 6H, H₄). ¹³C NMR (125 MHz, CDCl₃): δ 180.44 (s, C(carbene(bimy))), 160.62, 159.00 (s, C(benzene)), 145.17, 134.80, 137.36, 132.25, 124.49, 128.89, 126.60, 121.84, 121.83, 126.64, 119.24, 115.58, 54.58, 55.55, 53.79, 53.59, 36.99, 21.10, 20.16. HR-ESI-MS: m/z 770.0095 [8b + Na]⁺ (calcd for C₂₉H₃₄Br₃N₆O₂Pd).
Representative Procedure for the Skeletal Rearrangement of 9. Au(OtBu)₃ (0.063 mmol, 5 mol%) was added to a solution of 9b (30 mg, 0.126 mmol) in CH₂Cl₂ (1 mL). In a separate vial, silver hexafluoroantimonate (2.2 mg, 0.0063 mmol, 5 mol%) was dissolved in CH₂Cl₂ (0.1 mL), and then this solution was transferred to 9 and washed in with CH₂Cl₂ (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.39 IR: ν (cm⁻¹) 2954 w, 2917 w, 2853 w (C–H), 1655 w (C=C), 1604 w, 1496 m, 1453 m (aromatic C=C), 1107 s (C–O–C). ¹H NMR (400 MHz, CDCl₃): δ 7.31–7.15 (m, 5H, Ar–H), 5.40 (q, J = 6.2, 1.2 Hz, 1H, OCH₂CH₂), 4.00 (d, J = 6.2 Hz, 2H, OCH₂CH₂), 3.45 (t, J = 6.4 Hz, 2H, OCH₂CH₂), 2.65 (t, J = 7.4 Hz, 2H, CH₂CH₂PH), 1.77 – 1.58 (m, 5H, 7H, allyl CH₂ and C(Ph)), 1.06 (s, 9H, C(CH₃)₃). ¹³C NMR (75 MHz, CDCl₃): δ 172.8 (C), 138.9 (C), 135.8 (C), 124.6 (CH), 120.8 (CH), 59.5 (C), 33.0 (CH₃), 43.4 (CH₂), 40.4 (CH₂), 27.4 (CH₃), 20.0 (CH₃).

Representative Procedure for Allylic Etherification Reactions. The gold(I) catalyst (0.0058 mmol, 5 mol%) was added to a solution of allylic alcohol 12 (15 mg, 0.0117 mmol) and 4-phenylbutanol (13; 19.6 μL, 0.129 mmol, 1.1 equiv) in CH₂Cl₂ (0.1 mL). In a separate vial, silver hexafluoroantimonate (2.0 mg, 0.0058 mmol, 5 mol%) was dissolved in CH₂Cl₂ (0.1 mL). The reaction mixture 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.46 IR: ν (cm⁻¹) 3027 w, 2954 m, 2917 w, 2852 m (C–H), 1655 w (C=C), 1640 w, 1496 m, 1453 m (aromatic C=C), 1107 s (C–O–C). ¹H NMR (400 MHz, CDCl₃): δ 7.43–7.15 (m, 5H, Ar–H), 5.40 (q, J = 6.2, 1.2 Hz, 1H, OCH₂CH₂), 4.00 (d, J = 6.2 Hz, 2H, OCH₂CH₂), 3.45 (t, J = 6.4 Hz, 2H, OCH₂CH₂), 2.65 (t, J = 7.4 Hz, 2H, CH₂CH₂Ph), 1.77 – 1.58 (m, 5H, 7H, allyl CH₂ and C(Ph)), 1.06 (s, 9H, C(CH₃)₃). ¹³C NMR (75 MHz, CDCl₃): 138.9 (C), 135.8 (C), 124.6 (CH), 120.8 (CH), 59.5 (C), 33.0 (CH₃), 43.4 (CH₂), 40.4 (CH₂), 27.4 (CH₃), 20.0 (CH₃).
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