ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Synthesis, Characterization, and Catalytic Activity of Cationic NHC Gold(III) Pyridine Complexes

Serena Orbisaglia,[†,§] Béatrice Jacques,[†] Pierre Braunstein,[†] Damien Hueber,[‡] Patrick Pale,[‡] Aurélien Blanc,*[,‡] and Pierre de Frémont*[,†]

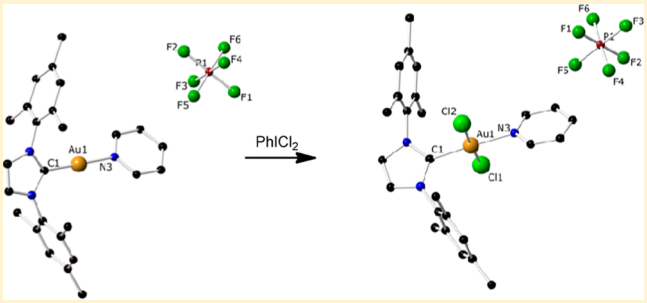
[†]Laboratoire de Chimie de Coordination, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 Rue Blaise Pascal, CS 90032, 67081 Strasbourg, France

[‡]Laboratoire de Synthèse, Réactivité Organique et Catalyse, Institut de Chimie (UMR 7177 CNRS), Université de Strasbourg, 4 Rue Blaise Pascal, CS 90032, 67081 Strasbourg, France

[§]School of Science and Technology, Università degli Studi di Camerino, Via S. Agostino 1, 62032 Camerino MC, Italy

Supporting Information

ABSTRACT: A series of cationic gold(I/III) pyridine complexes of the type $[(L)Au(pyr)](PF_6)$ and $[(L)AuCl_2(pyr)](PF_6)$, where L = IPr, (**1**, **5**); L = IMes (**2**, **6**); L = I^{t}Bu, (**3**, **7**); L = ICy (**4**, **8**); and L = PPh_3, (**9**, **10**), were synthesized and characterized by NMR spectroscopy and single-crystal X-ray diffraction. The stability of the new complexes and their catalytic activity in five well-established organic transformations were assessed.



INTRODUCTION

Since the isolation of the first stable N-heterocyclic carbene (NHC) by Arduengo in 1991,[1] these ligands became extremely popular to design a wide variety of transition metal complexes with enhanced stability and catalytic activities.[2] Without a doubt, organogold chemistry has taken full advantage of the easy use of NHCs. Indeed, these ligands with their strong electron donor ability and easy tuning of their steric properties, are able to stabilize the carbophilic gold centers in various oxidation states, by forming robust gold−carbon bonds.[3] This has recently allowed significant achievements in organogold chemistry, and various complexes initially thought to be elusive could be isolated and structurally characterized. Such examples include cationic NHC-Au(I) complexes, bearing neutral and weakly coordinated groups such as solvent molecules (MeCN, THF, DMSO),[4] alkenes,[5] alkynes,[6] allenes,[7] diimines,[8] carbon monoxide,[9] ammonia,[10] or silver chloride,[11] and neutral complexes with uncommon anionic groups such as fluoride,[12] hydroxide,[13] hydride,[14] triflimidate,[15] trifluoromethoxyde,[16] or acetylides.[17] Another interesting feature of the NHC-Au(I) cationic fragment, similar to that of the ubiquitous (phosphine)-Au(I) cation, is its isolobal character[18] with H^+, which was elegantly exploited by Sadighi et al. for the synthesis of digold hydride [Au_2H core] or trigold [Au_3 core] cationic clusters.[14,19] In comparison, the organometallic chemistry of gold(III) with NHCs appears less developed than for gold(I) and is mainly restricted to neutral trichloride/tribromide Au(III) complexes whose NHC ligands differ only by the steric bulk associated with the N-alkyl/aryl groups.[20] In this regard, the recent reports of NHC-Au(III) moieties bound to fluoride,[21] diphenylpyridine,[22] or triflimidate groups[23] indicate a first step toward the elaboration of more sophisticated complexes while, in parallel, differently functionalized carbene ligands with potentially chelating arms (e.g., picoline,[24] dialkylamine,[25] pyrazole,[26] pyridine[27]) are also being applied successfully to gold(III) chemistry. It is important to keep in mind that the organometallic chemistry around the gold(III) centers can be severely hampered by reductive elimination processes.

In parallel to the development of a broad library of NHC-gold(I/III) complexes, numerous applications in homogeneous catalysis[28] or medicinal chemistry[29] have blossomed. Usually, the NHC-Au fragment can act as a soft Lewis acid tolerant to most oxygen-based organic functions due to its low oxophilicity. Moreover, the gold centers stabilized by NHC ligands can smoothly undergo a reversible two-electron redox cycle—Au(I)/(III)—of catalytic relevance.[30] Gold complexes have become valuable tools in organic synthetic chemistry, promoting a broad range of remarkable reactions including the cycloisomerization of enynes,[31] the cyclization of allenes,[32] oxyarylations of alkenes,[33] hydroarylations,[34] hydroaminations,[35] glycosilations,[36] and, in general, the activation of alkene and alkyne functions toward the additions of nucleophiles.[28] Herein, we describe the synthesis and characterization of a new series of stable, cationic NHC gold(III) pyridine complexes, as well as their catalytic activity in five well-established gold-mediated transformations, including the halogenation of aromatic compounds by *N*-halosuccinimides,[37] the

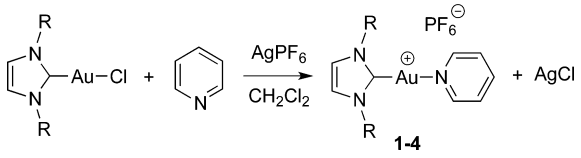
Received: April 19, 2013
Published: July 29, 2013

cycloisomerization of propargylic amides,[38] the Meyer−Schuster rearrangement of propargylic alcohols,[39] the [3+3]-rearrangement and Nazarov tandem reactions of enynyl acetates,[40] and the double hydroarylation of diyne diethers.[41]

RESULTS AND DISCUSSION

Synthesis of the Au(I) Complexes. The previously reported complex [(IPr)Au(Pyr)](PF$_6$) (**1**)[4b] (IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) was synthesized first, followed by the new complexes [(IMes)Au(Pyr)](PF$_6$) (**2**) (IMes = *N*,*N*′-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), [(I^{t}Bu)Au(Pyr)](PF$_6$) (**3**) (I^{t}Bu = *N*,*N*′-bis(*tert*-butyl)-imidazol-2-ylidene), and [(ICy)Au(Pyr)](PF$_6$) (**4**) (ICy = *N*,*N*′-bis(cyclohexyl)imidazol-2-ylidene). The syntheses were carried out using 10 equiv of pyridine and 1 equiv of silver hexafluorophosphate (AgPF$_6$) as halide abstractor in CH_2Cl_2, a non-coordinating solvent. All complexes were obtained in yields above 89% (Scheme 1).

Scheme 1. Synthesis of the [(NHC)Au(Pyr)](PF$_6$) Complexes 1−4



Their ^{1}H NMR spectra clearly exhibit all the expected signals, and the coordination of the pyridine to the gold(I) center is easily evidenced by a downfield shift (between 0.3 and 0.5 ppm) of the signals related to its *para*- and *meta*-proton(s). Furthermore, the resonance of the *ortho*-protons is upfield shifted by 0.5 ppm upon coordination for **1** and **2** but remains unchanged for **3** and **4**. The ^{13}C NMR spectra display the characteristic signals of the carbene carbon of a cationic NHC-Au(I) fragment bound to a nitrogen ligand, with chemical shifts in the range 166.2−160.2 ppm. The ^{31}P and ^{19}F NMR spectra are in good agreement with the presence of PF_6^-, exhibiting a septet at −144.5 ppm and a doublet at −73.5 ppm, respectively. After two days in solution, in nondry CH_2Cl_2, no change of the ^{1}H and ^{13}C spectra is noticeable, while the ^{31}P spectra reveal the presence of $PO_2F_2^-$ formed by hydrolysis of PF_6^-. The complexes **2**−**4** were crystallized by slow evaporation of acetone/petroleum ether solutions, and their structures were determined by single-crystal X-ray diffraction. The complexes crystallize in the $P2_1/c$, $P2_1/c$, and $P\bar{1}$ space groups, respectively. The unit cell of **4** contains also four well-ordered molecules of cocrystallized acetone in strong interaction with the PF_6^- anions. All the complexes display a cationic gold(I) center in a nearly linear coordination environment with the C−Au−N angles comprised between 176.2(2)° and 179.1(5)°. The C−Au bond lengths are in the range 1.979(6)−1.988(8) Å and are similar to those found in the corresponding neutral complexes [(NHC)AuCl].[42] The N−Au bond lengths, between 2.058(5) and 2.060(6) Å, are in the range of values found for gold complexes with pyridine donor ligands.[4b,43] As expected, the PF_6^- anions do not interact with the gold(I) centers, but they ensure crystal stability through multiple H···F bonds (Figure 1).

Synthesis of the Au(III) Complexes. The complexes **1**−**4** were dissolved in CH_2Cl_2, and a slight excess of iodobenzene dichloride (1.05 equiv) was added at room temperature to perform their oxidation to the corresponding cationic complexes [(IPr)AuCl$_2$(Pyr)](PF$_6$) (**5**), [(IMes)AuCl$_2$(Pyr)](PF$_6$) (**6**), [(I^{t}Bu)AuCl$_2$(Pyr)](PF$_6$) (**7**), and [(ICy)AuCl$_2$(Pyr)](PF$_6$) (**8**), respectively. After it was stirred for 3 h, the reaction mixture turned yellow. Upon filtration over a plug of Celite and precipitation with pentane, the new complexes were cleanly recovered in excellent yields (above 84%) (Scheme 2).

Their ^{1}H NMR spectra show a significant downfield shift (+0.3 ppm) for the signals associated with the imidazole backbone and the *ortho*-protons from the pyridine ring compared to the starting NHC-Au(I)-pyridine complexes. The isopropyl proton (septet) signal of **5**, which is very sensitive to the gold environment, is also shifted from 2.56 to 2.79 ppm, in good agreement with the formation of a (IPr)Au(III) fragment. The oxidation to gold(III) is further confirmed by the ^{13}C NMR spectra of **5**−**8**, which exhibit a significant upfield shift (between −35 and −40 ppm) for the carbenic carbons signals. Their values range from 120.0 to 131.6 ppm and are very close to those reported for the related [(NHC)AuCl$_2$(NTf$_2$)] complexes.[23] The ^{31}P NMR spectra confirm the cationic character of **5**−**8** with the presence of the PF_6^- anion. The arrangement of two symmetrical Cl$_{cis}$ ligands around the gold center is confirmed by

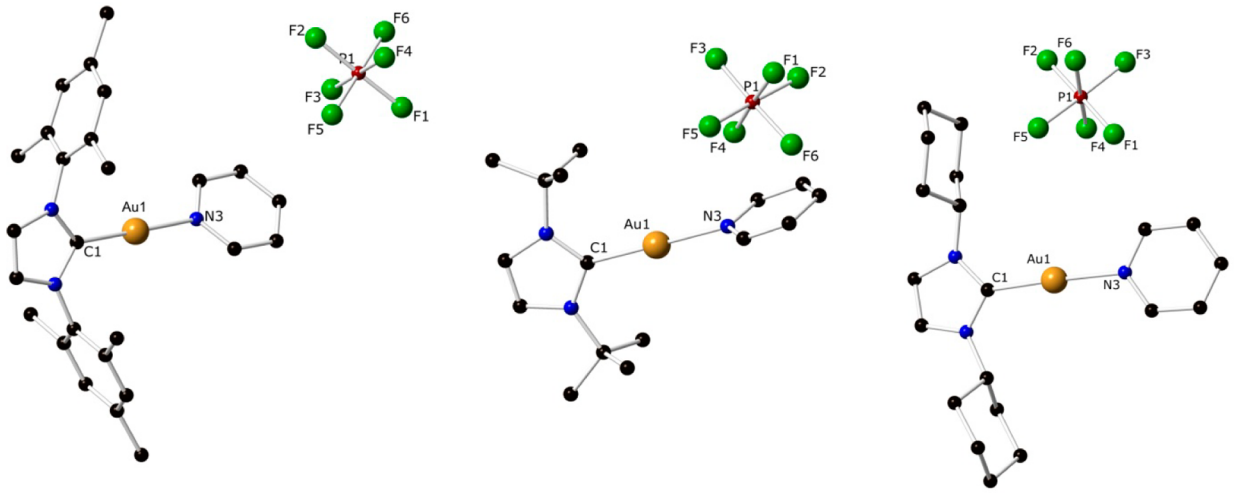
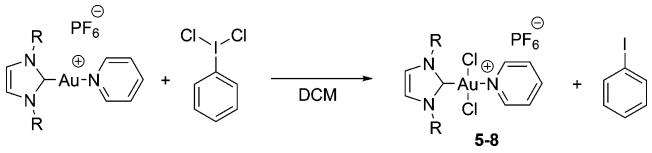


Figure 1. Ball-and-stick representation of [(IMes)Au(pyr)](PF$_6$) (**2**), [(ICy)Au(pyr)](PF$_6$) (**3**), and [(I^{t}Bu)Au(pyr)](PF$_6$) (**4**). Hydrogen atoms have been omitted for clarity.

dx.doi.org/10.1021/om400338k | *Organometallics* 2013, 32, 4153−4164

Scheme 2. Synthesis of the $[(NHC)AuCl_2(Pyr)](PF_6)$ Complexes 5−8



the appearance in the infrared spectrum of an intense ν(Au−Cl) absorption band between 372 and 385 cm^{-1}.[44] These complexes were quantitatively crystallized by slow evaporation of their solutions in acetone and petroleum ether. Their structures were unambiguously characterized by single-crystal X-ray diffraction studies. The complexes **5**−**8** crystallize in the *F*2dd, $P2_1/c$, $P2_1/c$, and $P\bar{1}$ space groups, respectively. The large unit cell of **5** contains also 12 molecules of cocrystallized acetone molecules in strong interaction with 16 PF_6^- anions (2 PF_6^- and 1.5 acetone molecules per asymmetric unit, with Z = 8 via symmetry operations). All the gold(III) centers exhibit the expected square-planar coordination environment with the pyridine in *trans*-position to the NHC ligand, the C−Au−N angles being comprised between 176.1(3)° and 178.7(5)°. All other interligand angles are very close to 90° with maximum deviations of −2.8° and +3.3°. The Au−C distances, in the range 1.997(4)−2.012(6) Å, are in good agreement with the Au(III)−C distances found in related NHC complexes.[20a,46] The Au−N distances, in the range 2.076(3)−2.094(5) Å, are slightly longer than in the parent NHC-Au(I)-pyridine complexes, but in good agreement with those in other Au(III)-pyridine complexes.[45] The PF_6^- anions do not interact with the gold(III) center but ensure a good crystal cohesion through multiple H···F bonds (Figures 2, 3). In contrast to the cationic *cis*-pyridine-functionalized NHC gold(III) complexes reported by the Monkowius, Cadierno, and Helaja groups,[24,27b,c] the complexes **5**−**8** display a very selective substitution on the *trans*-position.

These new NHC-Au(III) complexes are air and light stable, both in solution and in the solid state. Preliminary studies performed in $CDCl_3$ unveiled a partial and slow conversion of **5** to $[IPrAuCl_3]$, which was detected by ^1H NMR and also isolated as a new crystalline polymorph.[46,47] By prior filtration of the chloroform through a plug of alumina to remove any trace of HCl, the formation of $[IPrAuCl_3]$ could be avoided.

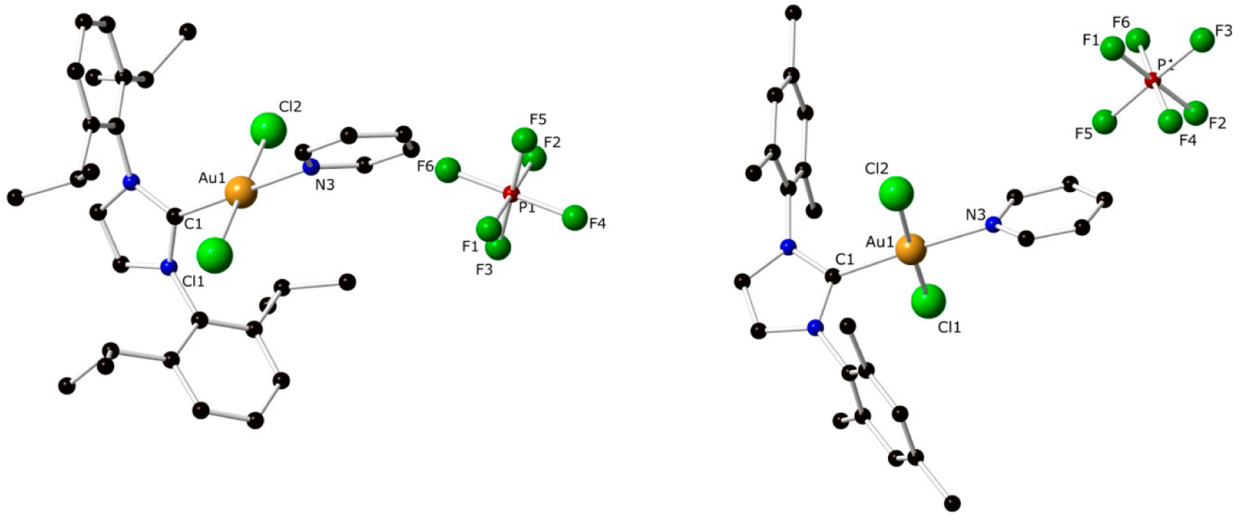


Figure 2. Ball-and-stick representation of $[(IPr)AuCl_2(pyr)](PF_6)$ (**5**) and $[(IMes)AuCl_2(pyr)](PF_6)$ (**6**). Hydrogen atoms have been omitted for clarity.

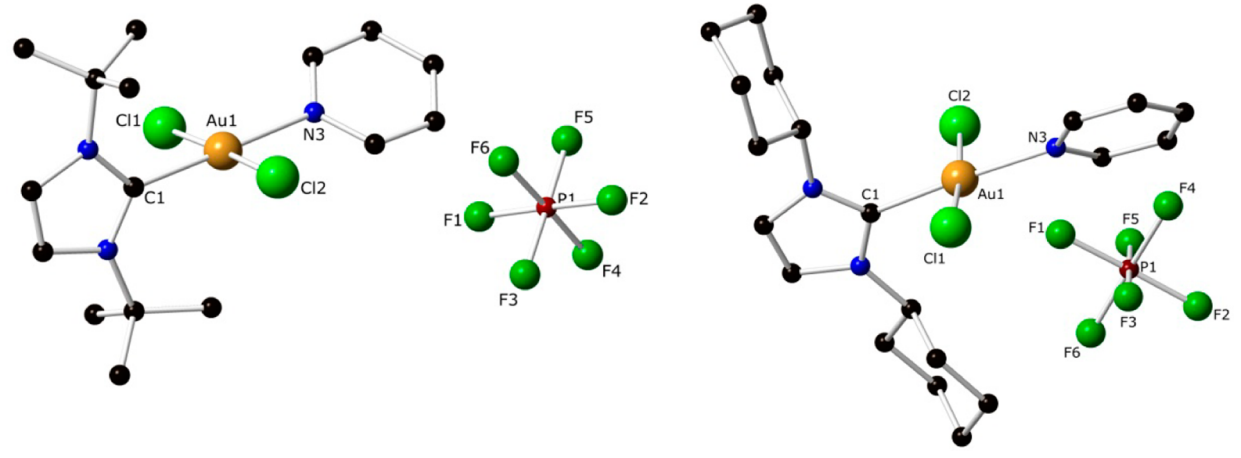


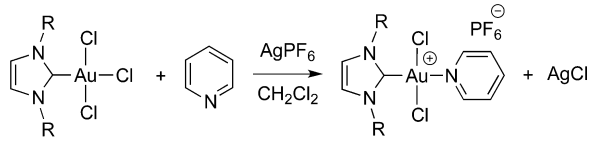
Figure 3. Ball-and-stick representation of $[(I^tBu)AuCl_2(pyr)](PF_6)$ (**7**) and $[(ICy)AuCl_2(pyr)](PF_6)$ (**8**). Hydrogen atoms have been omitted for clarity.

dx.doi.org/10.1021/om400338k | *Organometallics* 2013, 32, 4153−4164

Clearly, the cationic NHC-gold(III) fragment exhibits a high halide affinity.

The complexes **5**–**8** could also be obtained in excellent yields starting from the previously reported $[(NHC)AuCl_3]$ complexes[46] and by abstracting one chloride ligand in the presence of 10 equiv of pyridine and 1 equiv of $TlPF_6$ or $AgPF_6$. Interestingly, this synthetic approach is slightly more efficient (better yield) than the one involving direct oxidation of the pyridine gold(I) complexes. Once again, the pyridine ligand selectively occupies the *trans*-position with respect to the NHC ligand (Scheme 3).

Scheme 3. Alternative Synthesis of the $[(NHC)AuCl_2(Pyr)](PF_6)$ Complexes 5–8



5-8

Finally, the reaction of $[(IPr)AuCl_3]$ with 10 equiv of pyridine and 3.5 equiv of $AgPF_6$ was undertaken overnight at room temperature or in refluxing CH_2Cl_2 with the objective to form $[(IPr)Au(Pyr)_3](PF_6)_3$. The reaction mixture was then filtered over Celite and precipitated by addition of pentane to yield a clear yellow powder. The ^1H NMR spectrum revealed the formation of the complex $[(IPr)AuCl_2(Pyr)](PF_6)$ (**5**) together with a new pyridine-containing species integrating for three versus **5** and exhibiting signals at 8.62 and 8.01 ppm. This second species does not affect the symmetry of **5** by being in close contact, ruling out any equilibrium process with the pyridine bound to gold. The ^{13}C NMR spectra confirmed also the formation of **5** and of another pyridine adduct with signals at 152.0, 140.3, and 126.3 ppm. Recently Lee et al. reported the synthesis and characterization of $[(Pyr)_2Ag]_2(PF_6)_2$ by direct addition of pyridine to $AgPF_6$.[48] Pleasingly, this complex exhibits a very close ^1H NMR signature (signals shifted by less than 0.06 ppm) with the product found with **5**, whereas both ^{13}C NMR spectra match perfectly. Moreover, the elemental analysis of the powdery reaction product confirms the presence of a mixture of 1 $[(IPr)AuCl_2(Pyr)](PF_6)$ (**5**)/0.75 $[(Pyr)_2Ag]_2(PF_6)_2$, in good agreement with the latter species integrating for three pyridine versus **5**. It is very likely that $[(Pyr)_2Ag]_2(PF_6)_2$ and **5** have a similar solubility in CH_2Cl_2 and pentane and were not separated during the workup. Attempts to use more forcing reaction conditions (boiling acetonitrile) resulted in a slow decomposition to $[(IPr)AuCl]$ (30%) after 2 days (Scheme 4).

Thus, replacement of one or both *cis*-chloride ligands from **5** by pyridine was not successful. This contrasts with the easy formation of the cationic pincer-NHC-pyridine gold(III) complexes for which the pyridine-arm coordinates the gold center in *cis*-position under very mild conditions,[24,27b,c] but remains consistent with the lack of reactivity of $[(IPr)AuCl_2(NTf_2)]$ toward excess $Ag(NTf_2)$.[23]

Phosphine Pyridine Complexes. With the phosphine gold(I)/(III) complexes being also extremely popular and efficient homogeneous catalysts, the synthesis of $[(PPh_3)AuCl_2(Pyr)](PF_6)$ (**10**) was attempted for the sake of comparison with the NHC series. The same synthetic strategies as for **5**–**8** were employed. The reaction of $[(PPh_3)AuCl]$ with 1 equiv of $Ag/TlPF_6$ in the presence of excess pyridine led to $[(PPh_3)Au(Pyr)](PF_6)$ (**9**) in high yield, following a protocol described by Schmidbaur et al. for $[(PPh_3)Au(Pyr)](BF_4)$ and $[(PPh_3)Au(2\text{-hydroxy-Pyr})](BF_4)$.[43a] The ^{31}P NMR of **10** exhibits a signal at 29.2 ppm slightly shifted compared to $[(PPh_3)AuCl]$ (33.1 ppm) but in the range found for other cationic gold(I) phosphine pyridine complexes. Surprisingly, the CSD does not seem to contain any structural report for **9**; thus single crystals suitable for X-ray diffraction were grown from a solution mixture of CH_2Cl_2 and octane. Complex **9** crystallizes in the $P\bar{1}$ space group. The unit cell contains also two molecules of cocrystallized CH_2Cl_2 in interaction with the PF_6^- anions. The gold(I) center is in a linear coordination environment with a P–Au–N angle equal to 178.2(2)°. The P–Au and Au–N distances of 2.232(2) and 2.066(7) Å, respectively, are in good agreement with those in other gold(I) phosphine pyridine complexes (Figure 4).[4b,43]

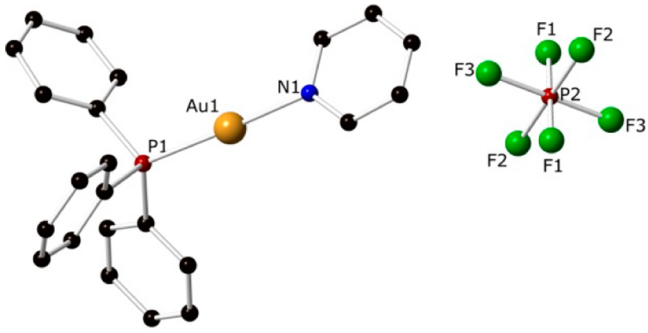
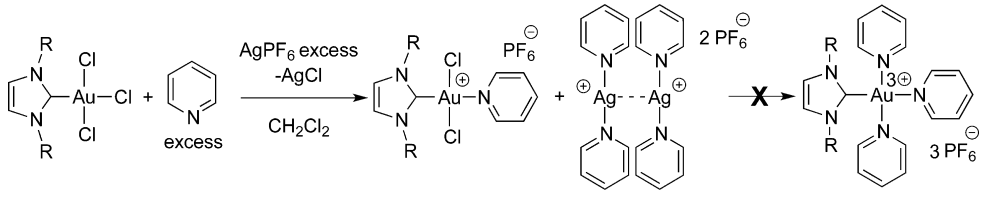


Figure 4. Ball-and-stick representation of $[(PPh_3)Au(pyr)](PF_6)$ (**9**). Hydrogen atoms have been omitted for clarity.

The oxidation of **9** with a slight excess of iodobenzene dichloride (1.05 equiv) was attempted in dry CH_2Cl_2 under protection from light and led to a yellow solution. The ^1H NMR spectrum displays a complicated pattern in the aromatic region with indications of dynamic processes. The complete reduction of $PhICl_2$ proceeds cleanly, as evidenced by the formation of iodobenzene. Two types of pyridine compounds (P1/P2) (with signals different from those of the free pyridine) are observable and display signals at 8.89 (H-*ortho*), 8.18 (H-*para*), below 7.8 ppm, and being hidden (H-*meta*) for P1 and at 8.74 (H-*ortho*), 8.51 (H-*para*), and 8.01 ppm (H-*meta*) for P2. After 5 min reaction time, the ratio P1/P2 is equal to 9:1, after 2.5 h it

Scheme 4. Attempted Syntheses of $[(IPr)Au(Pyr)_3](PF_6)_3$



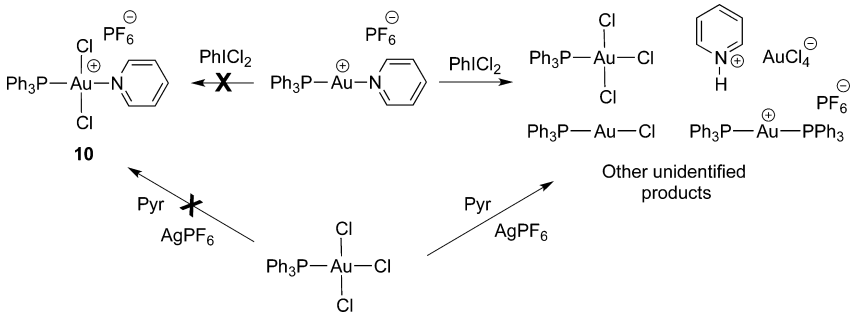
dx.doi.org/10.1021/om400338k | Organometallics 2013, 32, 4153–4164

becomes 5:5, and finally after 3 days the ratio is 0:10. Interestingly, the signals of P1 match perfectly with those of [(Pyr)$AuCl_3$].[49] The other aromatic signals account for at least two types of triphenylphosphine-containing compounds. Importantly, there is no trace of the starting complex **9**. After 5 min, the ^{31}P NMR spectrum displays an intense peak at 41.0 ppm, which was not assigned, and two minor peaks at 44.0 and 32.7 ppm. Whereas the latter can be assigned to [(PPh_3)AuCl], the former could be due to either [(PPh_3)$AuCl_3$] or [$(PPh_3)_2$Au](PF_6),[50] since these complexes have very similar resonances at 44.0 and 44.9 ppm. The situation being similar to the ^1H NMR spectra, these products cannot be unambiguously discriminated. The ratio of [(PPh_3)AuCl] and [(PPh_3)$AuCl_3$] or [$(PPh_3)_2$Au](PF_6) increases with time and the signal at 41.0 ppm fades until complete disappearance after 2.5 h. Attempts to crystallize the reaction mixture yielded yellow and colorless crystals, which confirmed the formation of [(PPh_3)$AuCl_3$] and [(PPh_3)AuCl].

The synthesis of [(PPh_3)$AuCl_2$(pyr)](PF_6) (**10**) was then attempted by reacting 3.5 equiv of pyridine with [(PPh_3)$AuCl_3$] in the presence of 1 equiv of $AgPF_6$. After 5 min, once again the aromatic region of the ^1H NMR spectra indicates the presence of different PPh_3-containing compounds. Most of the pyridine is uncoordinated, there is only a trace of a second pyridine species (1%) with signals at 8.89, 8.17, and 8.01 ppm, which does not account for the formation of **9**. After 2 h, the ^1H NMR spectrum does not present any significant change. The ^{31}P NMR spectrum reveals two species at 33.1 and 29.9 ppm. It confirms also the disappearance of [(PPh_3)$AuCl_3$] within 5 min. Once again, the species with the resonance at 33.1 ppm is likely to be [(PPh_3)AuCl], whereas the species at 29.9 ppm might be either [$(PPh_3)_2$Au]Cl or PPh_3=O owing to some trace of water appearing with time.[51] It is also important to note that all the syntheses based on the gold(I/III) phosphine systems led ultimately to the appearance of colloids or of a gold mirror. As it is known that [(PPh_3)$AuCl_3$] is prompt to decompose,[52] a solution of [(PPh_3)$AuCl_3$] containing 3.5 equiv of pyridine was prepared in CD_2Cl_2 and kept cold (with dry ice) in the dark, to ensure its stability prior to addition of the silver salt. After 15 min, its ^{31}P NMR spectrum showed already the formation in very small quantities of two new products with signals at 33.1 and 27.3 ppm, assigned to [(PPh_3)AuCl] and likely PPh_3=O, respectively. After 3 h at low temperature, the concentration of both products increases slowly, the formation of [(PPh_3)AuCl] being the fastest. The ^1H NMR spectrum reveals that most of the pyridine is free, while a minor species (2% vs free pyridine) has signals at 8.89, 8.17, and 8.01 ppm. Then, warming up the solution to room temperature accelerates the formation of [(PPh_3)AuCl] and PPh_3=O. After 1.75 h, formation of a third species with a ^{31}P chemical shift at 65.9 ppm occurs. After 4 h, the formation of three minor products continues, while [(PPh_3)-$AuCl_3$] is half consumed. Finally after 4 days, the ^{31}P NMR shows the complete disappearance of [(PPh_3)$AuCl_3$] and of the species resonating at 65.9 ppm; the main product remains [(PPh_3)AuCl] with traces of PPh_3=O. As yellow crystals started to appear in the NMR tube, their study by X-ray diffraction revealed the formation of another decomposition product, [PyrH][$AuCl_4$].[53] From the different NMR studies performed, it appears clearly that the synthesis of **10** is highly challenging; the cationic phosphine gold(III) pyridine complexes would likely require more strongly donating phosphine ligands than PPh_3 in order to be thermodynamically viable (Scheme 5).[54]

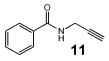
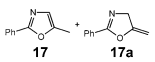
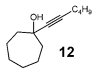
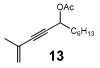
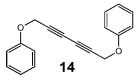
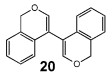
Catalytic Properties. The complexes [(IPr)$AuCl_2$(Pyr)]-(PF_6) (**5**) and [(I^tBu)$AuCl_2$(Pyr)](PF_6) (**7**) were tested for five, well-established gold-catalyzed transformations: the halogenation of aromatics by *N*-halosuccinimides (C-1), the cycloisomerization of propargylic amides (C-2), the Meyer–Schuster rearrangement of propargylic alcohols (C-3), the [3+3]-rearrangement and Nazarov tandem reactions of enynyl acetates (C-4), and finally the double hydroarylation of diyne diethers (C-5). Their activities were compared to those of the gold systems usually employed for these transformations by using similar experimental conditions (solvents, temperatures).[37−41] For C-1, the naphthalene can be fully converted in 15 h to 1-bromonaphthalene (**16**) with *N*-bromosuccinimide (NBS) in the presence of 0.1 mol % of $AuCl_3$ at 80 °C in dichloroethane (DCE).[37] The complexes **5** and **7** do not promote any reaction unless one equivalent of silver salt ($AgSbF_6$) is added. Once activated, the conversions, with 1 mol % of **5** or **7**, reach a maximum of 56% and 59%, respectively, after 20 h at 80 °C in DCE. They exhibit a poor activity compared to $AuCl_3$. For C-2, the *N*-(prop-2-yn-1-yl)benzamide **11** can be converted to 5-methyl-2-phenyloxazole **17** in 95% yield, in the presence of 5 mol % of $AuCl_3$ at 20 °C in CH_2Cl_2 for 12 h.[38] Upon activation with $AgSbF_6$, 5 mol % of **5** and **7** convert **11** in 76% and 75% yield, respectively, after 90 min in refluxing CH_2Cl_2. They exhibit a similar activity compared to $AuCl_3$. For C-3, the 1-(hex-1-yn-1-yl)cycloheptanol **12** can be converted in 3 h to 1-cycloheptylidenehexan-2-one in 80% yield in the presence of 2 mol % of [(PPh_3)Au(NTf_2)] at 20 °C in CH_2Cl_2.[39] Reaction C-3 is unknown with any gold(III) catalyst, and 5 mol % of **5** and **7** did not perform the desired transformation. Instead, the alcohol elimination product (hex-1-yn-1-ylcycloheptane) (**18a**) was quantitatively formed in 1 h at room temperature in CH_2Cl_2. For C-4, the 2-methylundec-1-en-3-yn-5-yl acetate **13** can be quantitatively converted to 3-hexyl-5-methylcyclopent-2-enone **19** in the presence of 1 mol % of [(PPh_3)AuCl]/$AgSbF_6$ at room temperature in CH_2Cl_2 in 30 min.[40] $AuCl_3$ can also mediate this transformation but with less efficiency, yielding 48% of **19** after 30 min.

Scheme 5. Decomposition Pathways upon the Attempted Syntheses of 10



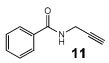
dx.doi.org/10.1021/om400338k | *Organometallics* 2013, 32, 4153−4164

Table 1. Summary of the Catalytic Results with [(IPr)AuCl$_2$(Pyr)](PF$_6$) (5) and [(I^{t}Bu)AuCl$_2$(Pyr)](PF$_6$) (7)

entry	substrate	catalyst[a] (mol%)	Conditions	product	time (h)	yield (%)
C-1		**5** (1)	dry CH_2Cl_2 80 °C	 **16**	20	56
		7 (1)			20	59
C-2	 **11**	**5** (5)	dry CH_2Cl_2 45 °C	 **17** **17a**	12	76[b]
		7 (5)			1.5	75[b]
C-3	 **12**	**5** (5)	-		1	elim.[c]
		7 (5)			1	elim.[c]
C-4	 **13**	**5** (5)	-	 **19**	1	75
		7 (5)			3	81
C-5	 **14**	**5** (5)	-	 **20**	4	70
		7 (5)			4	69

[a]Activated with $AgSbF_6$. [b]Mixture of 5-methyl-2-phenyloxazole **17** and 5-methylene-2-phenyl-4,5-dihydrooxazole **17a** (ratio 7:93 and 37:63, respectively). [c]Only the elimination product **18a** was formed (see Experimental Section).

Table 2. Summary of the Catalytic Tests with 1

entry	substrate	catalyst (mol%)	Conditions	product	time (h)	yield (%)
C-2	 **11**	**1** (5)	dry CH_2Cl_2, rt	 **17a**	4	77[a]
		1 (5)	$AgSbF_6$, dry CH_2Cl_2, rt		2.5	56[a]
C-4	 **13**	**1** (5)	dry CH_2Cl_2, 45°C	 **19**	4.5	72
		1 (5)	$AgSbF_6$, dry CH_2Cl_2 , rt		4.5	65

[a]No trace of isomerized product **17** was detected by ^{1}H NMR analysis.

Upon activation with $AgSbF_6$, 1 mol % of **5** and **7** convert **13** in 75% and 81% yield after 1 and 3 h, respectively, in refluxing CH_2Cl_2. Once again **5** and **7** are more sluggish than $AuCl_3$, but better yields are obtained. Finally, for C-5, the 1,6-diphenoxyhexa-2,4-diyne **15** was converted to 2*H*,2′*H*-4,4′-bichromene (**20**) in 95% yield in the presence of 5 mol % of [(PPh$_3$)AuCl]/$AgSbF_6$ after 20 min at 30 °C in CH_2Cl_2.[41] The reaction does not proceed with $AuCl_3$/AgOTf. Upon activation with $AgSbF_6$, 5 mol % of **5** and **7** convert **15** in 70% and 69% yield, respectively, after 4 h in refluxing CH_2Cl_2. Their activities are poorer compared to [(PPh$_3$)AuCl]/$AgSbF_6$ but better than with the $AuCl_3$/AgOTf system (Table 1).

The complexes **5** and **7** display poor to moderate activities compared to the reference systems for the five transformations studies. Surprisingly, they do not show any sign of activity in the absence of a silver salt. This may be related to recent mechanistic investigations by Shi et al., who have suggested an involvement of Au−Ag bimetallic catalysts.[55] It also emphasizes the difficulties in gaining a clear picture of the active species involved. A closer look at the ^{1}H NMR spectra of the crude reactions performed with 5% mol catalysts allows the detection of the catalyst fragments. C-1, C-3, and C-4 seem to proceed exclusively via some NHC-gold(III) fragments (including **5** and **7**), while C-2 and C-5 seem to involve exclusively some NHC-gold(I) fragments (including **1** and **3**). These results contrast with the inertness of **1** to promote the allylic acetate rearrangement[4a] and suggest a reaction pattern even more complicated than anticipated owing to the easy reduction of the gold(III) halide complexes.

To further confirm the catalytic potential of **1**, tests were made for C-2 and C-4. Complex **1** promotes C-2 and C-4 with a moderate activity, comparable to **5**, thus yielding exclusively **17a** and **19** in 77% and 72% yield, respectively. More interestingly, **1** was revealed to be equally active without addition of $AgSbF_6$ (Table 2). The ^{1}H NMR spectra of the crude reaction show the presence of only **1** for the catalysis made without silver and of **1** plus a second unidentified NHC-Au(I) species in the presence of $AgSbF_6$. These results hint at the possibility of using more often NHC-Au-pyridine systems in catalysis, in particular the gold(I) complexes, which are extremely stable. They also reveal the need for a better understanding of the role of the silver salts and of the changes in the gold coordination sphere to predict catalytic activity.

CONCLUSION

A series of new cationic gold(III) monopyridine NHC complexes was readily prepared in excellent yields. They were tested in five gold-mediated organic transformations and display poor to moderate catalytic activity compared to the reference systems. The gold(III) complexes strongly tend to be reduced under the catalytic conditions, thus complicating the reaction pattern. Moreover, the gold(III) complexes were inactive without addition of silver salt, while the parent gold(I) pyridine complexes did not require the use of silver salts. The synthesis of a bis- or *tris*-pyridine gold(III) NHC complexes failed, the reaction stopping after the formation of the monopyridine complex. Finally the related cationic gold(III) monopyridine PPh$_3$ complex was not accessible using the synthetic strategy used with the NHC ligands, and extensive decomposition or ligand redistribution products were observed.

dx.doi.org/10.1021/om400338k | *Organometallics* 2013, 32, 4153−4164

EXPERIMENTAL SECTION

General Considerations. Proton (^{1}H NMR), carbon (^{13}C NMR), phosphorus (^{31}P NMR), and fluorine (^{19}F NMR) nuclear magnetic resonance spectra were recorded on the following instruments: Bruker AVANCE I, 300 MHz spectrometer; Bruker AVANCE III, 400 MHz spectrometer; and Bruker AVANCE I, 500 MHz spectrometer, respectively. The chemical shifts are given in parts per million (ppm). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept. = septet, m = multiplet, b = broad), coupling constants (J/Hz), and integration. Assignments were determined on the basis of either unambiguous chemical shifts or coupling patterns. The residual solvent proton (^{1}H) or carbon (^{13}C) resonance, or the PF_6 anion signals (^{31}P, ^{19}F) were used as reference values. For ^{1}H NMR: $CDCl_3$ = 7.26 ppm, CD_2Cl_2 = 5.32 ppm. For $^{13}C\{^1H\}$ NMR: $CDCl_3$ = 77.1 ppm, CD_2Cl_2 = 53.8. For $^{31}P\{^1H\}$ NMR: PF_6^- = −141.3 ppm (sept., $^1J(^{31}P-^{19}F)$ = 712.0 Hz). For $^{19}F\{^1H\}$ NMR: PF_6^- = −74.0 ppm (d, $^1J(^{31}P-^{19}F)$ = 712.0 Hz). IR spectra were recorded in the region 4000−200 cm^{-1} on a Nicolet 6700 FT-IR spectrometer (ATR mode, diamond crystal). Elemental analyses were performed by the "Service de Microanalyses", Université de Strasbourg. For the X-ray diffraction studies, the intensity data were collected at 173(2) K on a Kappa CCD diffractometer 88 (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å). Crystallographic and experimental details for all the structures are summarized in the Supporting Information (p S13). The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97) with anisotropic thermal parameters for all the non-hydrogen atoms.[56] The hydrogen atoms were introduced into the geometrically calculated positions (SHELXL-97 procedures) and refined riding on the corresponding parent atoms.

Synthesis of the Gold Complexes. All reactions were carried out in air with nondried solvents, unless stated otherwise. CD_2Cl_2 was distilled from CaH_2, degassed, and stored over 4 Å molecular sieves. $PhICl_2$ was prepared following a procedure described by Kalyani and Sanford[57] and stored at −30 °C. The silver hexafluorophosphate was stored away from light under argon prior to use. All other reagents (including the pyridine) were used as received from commercial suppliers. All gold(III) complexes were made and kept in the dark. Yields of the new complexes are based on the precursor gold complexes.

*Synthesis of [(IMes)Au(Pyr)](PF$_6$) (**2**).* $AgPF_6$ (96 mg, 0.37 mmol, 1.0 equiv) was added to a solution of [(IMes)AuCl] (200 mg, 0.37 mmol, 1.0 equiv) and pyridine (0.30 mL, 3.7 mmol, 10 equiv) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature overnight and then filtered over Celite. The filtrate was added to pentane (30 mL), and the resulting precipitate was filtered, washed with pentane (3 × 10 mL), and dried under vacuum to afford **2** (240 mg, 0.33 mmol) as a white solid. Yield: 89%. ^{1}H NMR (CD_2Cl_2, 500 MHz): 8.06 (d, J = 7 Hz, 2H, $CH^{o\text{-}Py}$), 8.00 (t, J = 7 Hz, 1H, $CH^{p\text{-}Py}$), 7.55 (t, J = 7 Hz, 2H, $CH^{m\text{-}Py}$), 7.33 (s, 2H, $CH^{imidazole}$), 7.10 (s, 4H, CH^{Ar}), 2.38 (s, 6H, p-CH_3), 2.17 (s, 12H, o-CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz): 166.2 ($C^{carbene}$), 151.4 ($CH^{o\text{-}Py}$), 141.9 ($CH^{p\text{-}Py}$), 140.9 ($C^{p\text{-}Ar}$), 135.2 ($C^{o\text{-}Ar}$), 134.6 ($C^{i\text{-}Ar}$), 130.0 ($CH^{m\text{-}Ar}$), 127.2 ($CH^{m\text{-}Py}$), 124.2 ($CH^{imidazole}$), 21.3 (p-CH_3), 18.0 (o-CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4 MHz): −144.5 (sept., $^1J(^{31}P-^{19}F)$ = 710 Hz, PF_6^-). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 282.2 MHz): −73.5 (d, $^1J(^{19}F-^{31}P)$ = 710 Hz, PF_6^-). Anal. Calcd for $C_{26}H_{29}AuF_6N_3P$: C, 43.05; H, 4.03; N, 5.79. Found: C, 43.22; H, 4.13; N, 5.80.

*Synthesis of [(I^{t}Bu)Au(Pyr)](PF$_6$) (**3**).* A procedure similar to that used for compounds **2** gave **3** as a white solid (261 mg, 0.43 mmol). Yield: 89%. ^{1}H NMR (CD_2Cl_2, 300 MHz): 8.59 (d, J = 7 Hz, 2H, $CH^{o\text{-}Py}$), 8.16 (t, J = 7 Hz, 1H, $CH^{p\text{-}Py}$), 7.77 (t, J = 7 Hz, 2H, $CH^{m\text{-}Py}$), 7.29 (s, 2H, $CH^{imidazole}$), 1.92 (s, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz): 160.2 ($C^{carbene}$), 152.2 ($CH^{o\text{-}Py}$), 141.9 ($CH^{p\text{-}Py}$), 127.6 ($CH^{m\text{-}Py}$), 118.3 ($CH^{imidazole}$), 59.6 ($C(CH_3)_3$), 32.3 ($C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4 MHz): −144.5 (sept., $^1J(^{31}P-^{19}F)$ = 710 Hz, PF_6^-). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 282.2 MHz): −73.4 (d, $^1J(^{19}F-^{31}P)$ = 710 Hz, PF_6^-). Anal. Calcd for $C_{16}H_{25}AuF_6N_3P$: C, 31.96; H, 4.19; N, 6.99. Found: C, 32.25; H, 4.24; N, 7.02.

*Synthesis of [(ICy)Au(Pyr)](PF$_6$) (**4**).* A procedure similar to that used for compound **2** gave **4** as a white solid (177 mg, 0.27 mmol). Yield: 95%. ^{1}H NMR (CD_2Cl_2, 500 MHz): 8.61 (d, J = 7 Hz, 2H, $CH^{o\text{-}Py}$), 8.16 (t, J = 7 Hz, 1H, $CH^{p\text{-}Py}$), 7.76 (t, J = 7 Hz, 2H, $CH^{m\text{-}Py}$), 7.16 (s, 2H, $CH^{imidazole}$), 4.45−4.52 (m, 2H, CH^{Cy}), 2.12−2.17 (m, 4H, CH_2^{Cy}), 1.91−1.97 (m, 4H, CH_2^{Cy}), 1.69−1.80 (m, 6H, CH_2^{Cy}), 1.44−1.53 (m, 4H, CH_2^{Cy}), 1.22−1.31 (m, 2H, CH_2^{Cy}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz): 161.0 ($C^{carbene}$), 151.9 ($CH^{o\text{-}Py}$), 141.9 ($CH^{p\text{-}Py}$), 127.5 ($CH^{m\text{-}Py}$), 119.1 ($CH^{imidazole}$), 62.4 (CH^{Cy}), 34.7 (CH_2^{Cy}), 25.9 (CH_2^{Cy}), 25.4 (CH_2^{Cy}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4 MHz): −144.5 (sept., $^1J(^{31}P-^{19}F)$ = 710 Hz, PF_6^-). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 282.2 MHz): −73.3 (d, $^1J(^{19}F-^{31}P)$ = 710 Hz, PF_6^-). Anal. Calcd for $C_{20}H_{29}AuF_6N_3P$: C, 36.76; H, 4.47; N, 6.43. Found: C, 37.14; H, 4.60; N, 6.38.

*Synthesis of [(IPr)AuCl$_2$(Pyr)](PF$_6$) (**5**).* $PhICl_2$ (71 mg, 0.26 mmol, 1.05 equiv) was added to a solution of [(IPr)Au(Pyr)](PF_6) (200 mg, 0.25 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 3 h and then filtered through Celite. The filtrate was added to pentane (30 mL), and the resulting yellow precipitate was filtered, washed with pentane (3 × 10 mL), and dried under vacuum to afford **5** (188 mg, 0.21 mmol) as a yellow solid. Yield: 84%. ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.35 (d, J = 7 Hz, 2H, $CH^{o\text{-}Py}$), 8.12 (t, J = 7 Hz, 1H, $CH^{p\text{-}Py}$), 7.62−7.68 (m, 6H, $CH^{m\text{-}Py}$ and $CH^{imidazole}$ and $CH^{p\text{-}Ar}$), 7.45 (d, J = 8 Hz, 4H, $CH^{m\text{-}Ar}$), 2.79 (sept., J = 7 Hz, 4H, CH^{iPr}), 1.41 (d, J = 7 Hz, 12H, CH_3^{iPr}), 1.20 (d, J = 7 Hz, 12H, CH_3^{iPr}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz): 149.2 ($CH^{o\text{-}Py}$), 146.5 ($C^{o\text{-}Ar}$), 143.5 ($CH^{p\text{-}Py}$), 132.8 ($CH^{p\text{-}Ar}$), 132.0 ($C^{i\text{-}Ar}$), 131.6 ($C^{carbene}$), 128.6 ($CH^{imidazole}$), 128.0 ($CH^{m\text{-}Py}$), 125.4 ($CH^{m\text{-}Ar}$), 29.6 (CH^{iPr}), 26.7 (CH_3^{iPr}), 22.9 (CH_3^{iPr}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 162.0 MHz): −144.5 (sept., $^1J(^{31}P-^{19}F)$ = 710 Hz, PF_6^-). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 282.2 MHz): −73.4 (d, $^1J(^{19}F-^{31}P)$ = 710 Hz, PF_6^-). Anal. Calcd for $2(C_{32}H_{41}AuCl_2F_6N_3P)\cdot C_3H_6O$: C, 44.24; H, 4.88; N, 4.62. Found: C, 44.28; H, 4.92; N, 4.60. IR: ν(cm^{-1}): 385 (Au−Cl_{cis}).

*Synthesis of [(IMes)AuCl$_2$(Pyr)](PF$_6$) (**6**).* A procedure similar to that used for compound **5** gave **6** as a yellow solid (183 mg, 0.23 mmol). Yield: 82%. ^{1}H NMR (CD_2Cl_2, 300 MHz): 8.39 (d, J = 7 Hz, 2H, $CH^{o\text{-}Py}$), 8.12 (t, J = 7 Hz, 1H, $CH^{p\text{-}Py}$), 7.65 (t, J = 7 Hz, 2H, $CH^{m\text{-}Py}$), 7.58 (s, 2H, $CH^{imidazole}$), 7.13 (s, 4H, CH^{Ar}), 2.40 (s, 6H, p-CH_3), 2.28 (s, 12H, o-CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz): 149.4 ($CH^{o\text{-}Py}$), 143.4 ($CH^{p\text{-}Py}$), 142.1 ($C^{p\text{-}Ar}$), 135.8 ($C^{o\text{-}Ar}$), 132.4 ($C^{i\text{-}Ar}$), 130.7 ($C^{carbene}$), 130.5 ($CH^{m\text{-}Ar}$), 127.9 ($CH^{imidazole}$ or $CH^{m\text{-}Py}$), 127.8 ($CH^{imidazole}$ or $CH^{m\text{-}Py}$), 21.4 (p-CH_3), 18.7 (o-CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4 MHz): −144.5 (sept., $^1J(^{31}P-^{19}F)$ = 710 Hz, PF_6^-). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 282.2 MHz): −73.3 (d, $^1J(^{19}F-^{31}P)$ = 710 Hz, PF_6^-). Anal. Calcd for $C_{26}H_{29}AuCl_2F_6N_3P$: C, 39.21; H, 3.67; N, 5.28. Found: C, 39.06; H, 3.72; N, 5.24. IR: ν(cm^{-1}): 381 (Au−Cl_{cis}).

*Synthesis of [(I^{t}Bu)AuCl$_2$(Pyr)](PF$_6$) (**7**).* A procedure similar to that used for compound **5** gave **7** as a yellow solid (531 mg, 0.79 mmol). Yield: 95%. ^{1}H NMR (CD_2Cl_2, 500 MHz): 8.90 (d, J = 7 Hz, 2H, $CH^{o\text{-}Py}$), 8.28 (t, J = 7 Hz, 1H, $CH^{p\text{-}Py}$), 7.86 (t, J = 7 Hz, 2H, $CH^{m\text{-}Py}$), 7.70 (s, 2H, $CH^{imidazole}$), 2.00 (s, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz): 150.0 ($CH^{o\text{-}Py}$), 143.4 ($CH^{p\text{-}Py}$), 128.3 ($CH^{m\text{-}Py}$), 124.4 ($CH^{imidazole}$), 120.0 ($C^{carbene}$), 63.2 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4 MHz): −144.5 (sept., $^1J(^{31}P-^{19}F)$ = 710 Hz, PF_6^-). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 282.2 MHz): −73.3 (d, $^1J(^{19}F-^{31}P)$ = 710 Hz, PF_6^-). Anal. Calcd for $C_{16}H_{25}AuCl_2F_6N_3P$: C, 28.59; H, 3.75; N, 6.25. Found: C, 28.74; H, 3.77; N, 6,25. IR: ν(cm^{-1}): 374 (Au−Cl_{cis}).

*Synthesis of [(ICy)AuCl$_2$(Pyr)](PF$_6$) (**8**).* A procedure similar to that used for compound **5** gave **8** as a yellow solid (238 mg, 0.33 mmol). Yield: 87%. ^{1}H NMR (CD_2Cl_2, 400 MHz): 9.04 (d, J = 8 Hz, 2H, $CH^{o\text{-}Py}$), 8.29 (t, J = 8 Hz, 1H, $CH^{p\text{-}Py}$), 7.86 (t, J = 8 Hz, 2H, $CH^{m\text{-}Py}$), 7.44 (s, 2H, $CH^{imidazole}$), 4.42−4.48 (m, 2H, CH^{Cy}), 2.20−2.27 (m, 4H, CH_2^{Cy}), 1.94−2.01 (m, 4H, CH_2^{Cy}), 1.66−1.83 (m, 6H, CH_2^{Cy}), 1.44−1.57 (m, 4H, CH_2^{Cy}), 1.24−1.35 (m, 2H, CH_2^{Cy}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125.7 MHz): 149.7 ($CH^{o\text{-}Py}$), 143.6 ($CH^{p\text{-}Py}$), 128.0 ($CH^{m\text{-}Py}$), 124.0 ($C^{carbene}$), 122.6 ($CH^{imidazole}$), 62.6 (CH^{Cy}), 33.9 (CH_2^{Cy}), 25.6 (CH_2^{Cy}), 25.1 (CH_2^{Cy}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.4

dx.doi.org/10.1021/om400338k | Organometallics 2013, 32, 4153−4164

MHz): −144.4 (sept., $^1J(^{31}P-^{19}F)$ = 710 Hz, PF_6^-). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 282.2 MHz): −73.0 (d, $^1J(^{19}F-^{31}P)$ = 710 Hz, PF_6^-). Anal. Calcd for $C_{20}H_{29}AuCl_2F_6N_3P$: C, 33.16; H, 4.04; N, 5.80. Found: C, 33.26; H, 4.17; N, 5.67. IR: $\nu(cm^{-1})$: 372 ($Au-Cl_{cis}$).

The complexes **5**−**8** were also obtained by following the second procedure described below for **5**.

*Synthesis of [(IPr)AuCl$_2$(Pyr)](PF$_6$) (**5**).* Solid $AgPF_6$ (35 mg, 0.14 mmol, 1 equiv) was added to a solution of [(IPr)$AuCl_3$] (100 mg, 0.14 mmol, 1 equiv) and pyridine (0.11 mL, 1.4 mmol, 10 equiv) in CH_2Cl_2 (5 mL). The reaction mixture was stirred at room temperature overnight and then filtered over Celite. The filtrate was added in pentane (30 mL). The resulting yellow precipitate was filtered, washed with pentane (3 × 10 mL), and dried under vacuum to afford **5** (120 mg, 0.13 mmol) as a yellow solid. Yield: 93%.

*Synthesis of [(PPh$_3$)Au(Pyr)](PF$_6$) (**9**).* A procedure similar to that used for compounds **2**−**4** gave **9** as a white solid (257 mg, 0.38 mmol). Yield: 95%. ^1H NMR (CD_2Cl_2, 300 MHz): 8.64 (d, J = 7 Hz, 2H, $CH^{o\text{-}Py}$), 8.15 (t, J = 7 Hz, 1H, $CH^{p\text{-}Py}$), 7.78 (t, J = 7 Hz, 2H, $CH^{m\text{-}Py}$), 7.68−7.56 (m, 15H, PPh_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): 151.4 ($CH^{o\text{-}Py}$), 142.2 ($CH^{p\text{-}Py}$), 134.6 (d, $^2J(^{13}C-^{31}P)$ = 13 Hz, $CH^{o\text{-}Ph}$), 133.2 (d, $^4J(^{13}C-^{31}P)$ = 3 Hz, $CH^{p\text{-}Ph}$), 130.1 (d, $^3J(^{13}C-^{31}P)$ = 12 Hz, $CH^{m\text{-}Ph}$), 127.3 ($CH^{m\text{-}Py}$), 127.2 (d, $^1J(^{13}C-^{31}P)$ = 66 Hz, $C^{i\text{-}Ph}$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 121.5 MHz): 29.2 (s, PPh_3), −144.5 (septet, $^1J(^{31}P-^{19}F)$ = 710 Hz, PF_6^-). $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 282.4 MHz): −73.2 (d, $^1J(^{19}F-^{31}P)$ = 710 Hz, PF_6^-). Anal. Calcd for $C_{23}H_{20}AuF_6NP_2$: C, 40.43; H, 2.95; N, 2.05. Found: C, 40.35; H, 3.00; N, 2.16.

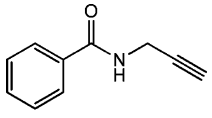
*Synthesis of [(PPh$_3$)AuCl$_2$(Pyr)](PF$_6$) (**10**).* $PhICl_2$ (63 mg, 0.23 mmol, 1.05 equiv) was added to a solution of [(PPh_3)Au(Pyr)](PF_6) (**9**) (150 mg, 0.22 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 3 h and then filtered through Celite. The filtrate was added to pentane (30 mL), and the resulting yellow precipitate was filtered, washed with pentane (3 × 10 mL), and dried under vacuum to afford a mixture of compounds.

*Synthesis of [(PPh$_3$)AuCl$_2$(Pyr)](PF$_6$) (**10**): NMR Studies.* $PhICl_2$ (4.0 mg, 0.16 mmol, 1.05 equiv) was added to a solution of [(PPh_3)Au(Pyr)](PF_6) (10 mg, 0.15 mmol, 1.0 equiv) in CD_2Cl_2 (1 mL). The reaction mixture was filtered through Celite and monitored over time.

*Synthesis of [(PPh$_3$)AuCl$_2$(Pyr)](PF$_6$) (**10**): NMR Studies.* $AgPF_6$ (5.0 mg, 0.02 mmol, 1.0 equiv) was added to a solution of [(PPh_3)$AuCl_3$] (10 mg, 0.02 mmol, 1.0 equiv) and pyridine (0.02 mL, 0.2 mmol, 10 equiv) in CD_2Cl_2 (3 mL). The reaction mixture was filtered through Celite and monitored over time.

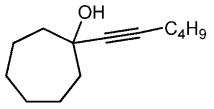
Homogenous Catalysis. Reagents and solvents were purified using standard methods. Dichloromethane and dichloroethane were distilled from CaH_2 under an argon atmosphere; pyrimidine was distilled from KOH; tetrahydrofuran (THF) was distilled from sodium metal/benzophenone and stored under an argon atmosphere. Anhydrous reactions were carried out in flame-dried glassware and under an argon atmosphere. All extractive procedures were performed using nondistilled solvents. Analytical thin layer chromatography (TLC) was carried out on silica gel 60 F254 plates with visualization by ultraviolet light, cerium ammonium molybdate, or potassium permanganate dip. Flash column chromatography was carried out using silica gel 60 (40−63 μm), and the procedure included the subsequent evaporation of solvents *in vacuo*.

*N-(Prop-2-yn-1-yl)benzamide (**11**).*[38] To a solution of propargylamine (12.7 mmol) in CH_2Cl_2 (28 mL) were added Et_3N



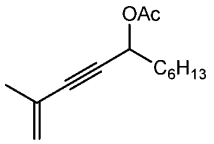
(14.0 mmol) at 0 °C and benzoyl chloride (19.1 mmol). The resulting mixture was stirred at room temperature for 2 h. The mixture was quenched with MeOH (19 mL), stirred for 1 h, and then evaporated. The crude was then taken in CH_2Cl_2 and 1 N $HCl_{(aq)}$ and extracted with CH_2Cl_2 (2×). The combined organic extracts were washed with brine, dried over $MgSO_4$, and evaporated. Flash column chromatography over silica gel (EA/cyclohexane 30%) gave the desired product **11** (1.828 g, 90%) as a white solid. TLC: R_f 0.63 (EA/cyclohexane 40%). ^1H NMR (300 MHz, $CDCl_3$): 2.29 (t, J = 2.6 Hz, 1 H), 4.26 (dd, J = 5.2, 2.6 Hz, 2 H), 6.29 (br, 1 H), 7.41−7.55 (m, 3 H), 7.75−7.82 (m, 2 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 29.9, 72.0, 79.5, 127.0, 128.7, 131.9, 133.7, 167.1.

*1-(Hex-1-yn-1-yl)cycloheptanol (**12**) (ref 39).* To a solution of ^{n}BuLi (1.6 M in hexanes, 6.1 mmol) in THF (10 mL) was added

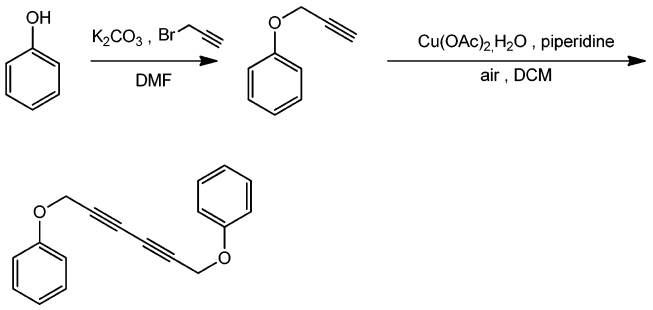


1-hexyne (6.1 mmol) at −78 °C under argon. The resulting mixture was stirred at this temperature for 15 min and was then allowed to warm to −20 °C over 5 min. Cycloheptanone (6.1 mmol) was then added at −78 °C. The reaction mixture was stirred for 30 min at −78 °C, then allowed to reach room temperature, and further stirred for 30 min (monitored by TLC). The mixture was quenched with a saturated NH_4Cl solution and extracted with Et_2O (2×). The combined organic extracts were dried over $MgSO_4$ and evaporated. Flash column chromatography over silica gel (EA/cyclohexane 10%) gave the desired product **12** (1.041 g, 88%) as a colorless oil. TLC: R_f 0.40 (EA/cyclohexane 20%). ^1H NMR (300 MHz, $CDCl_3$): 0.90 (t, J = 7.2 Hz, 3 H), 1.34−1.67 (m, 12 H), 1.72−1.84 (m, 3 H), 1.86−2.00 (m, 2 H), 2.20 (t, J = 7.0 Hz, 2 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 13.6, 18.3, 21.9, 22.3, 27.9, 30.9, 43.4, 71.9, 84.0, 82.9.

*2-Methylundec-1-en-3-yn-5-yl Acetate (**13**).*[58] To a solution of ^{n}BuLi (1.6 M in hexanes, 7.6 mmol) in THF (10 mL) was added

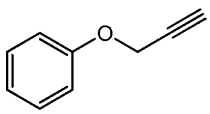


2-methyl-1-buten-3-yne (7.6 mmol) at −78 °C under argon. The resulting mixture was stirred at this temperature for 15 min and was then allowed to warm to −20 °C over 5 min. Heptanal (7.6 mmol) was then added at −78 °C. The reaction mixture was stirred for 30 min at −78 °C, then allowed to reach room temperature, and further stirred for 1.5 h (monitored by TLC). The mixture was quenched with Ac_2O (25 mmol) and stirred at 0 °C for 2 h. A saturated NH_4Cl solution was then added, and the mixture was extracted with Et_2O (2×). The combined organic extracts were dried over $MgSO_4$ and evaporated. Flash column chromatography over silica gel (EA/cyclohexane 5%) gave the desired product **13** (0.953 g, 56%) as a yellowish oil. TLC: R_f 0.58 (EA/cyclohexane 20%). ^1H NMR (300 MHz, $CDCl_3$): 0.87 (t, J = 6.7 Hz, 3 H), 1.28−1.42 (m, 8 H), 1.72−1.80 (m, 2 H), 1.87 (s, 3 H), 2.07 (s, 3 H), 5.23 (m, 1 H), 5.30 (m, 1 H), 5.48 (t, J = 6.6 Hz, 1 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 14.1, 21.2, 22.6, 23.4, 25.0, 28.8, 31.7, 34.9, 64.5, 85.6, 86.4, 122.7, 126.1, 170.1.



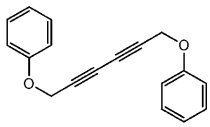
*(Prop-2-yn-1-yloxy)benzene (**14**).*[41] To a solution of phenol (63.8 mmol) in DMF (60 mL) were added K_2CO_3 (127.5 mmol) and propargyl bromide (80 wt % in toluene, 95.6 mmol). The resulting mixture was stirred at room temperature overnight. Water was then added, and the mixture was extracted with Et_2O (3×). The combined

dx.doi.org/10.1021/om400338k | Organometallics 2013, 32, 4153−4164



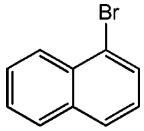
organic extracts were washed with water and brine, dried over $MgSO_4$, and evaporated. Flash column chromatography over silica gel (EA/cyclohexane 10%) gave the desired product **14** (7.426 g, 88%) as a yellow oil. TLC: R_f 0.68 (EA/cyclohexane 20%). ^{1}H NMR (400 MHz, $CDCl_3$): 2.52 (t, J = 2.4 Hz, 1 H), 4.70 (d, J = 2.4 Hz, 2 H), 6.95−7.04 (m, 3 H), 7.27−7.35 (m, 2 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 58.8, 75.4, 78.7, 114.9, 121.6, 129.5, 157.6.

*1,6-Diphenoxyhexa-2,4-diyne (**15**) (ref 41).* To a solution of (prop-2-yn-1-yloxy)benzene (**14**) (28.0 mmol) in CH_2Cl_2 (55 mL)



was added pyrimidine (28.0 mmol) and $Cu(OAc)_2{\cdot}H_2O$ (2.8 mmol). The resulting mixture was stirred at room temperature overnight under air (open flask). The mixture was then filtered over a pad of Celite, washed with water and saturated NH_4Cl solution, dried over $MgSO_4$, and evaporated. Flash column chromatography over silica gel (EA/cyclohexane 5%) gave the desired product **15** (2.164 g, 55%) as a yellowish solid. TLC: R_f 0.34 (EA/cyclohexane 5%). ^{1}H NMR (300 MHz, $CDCl_3$): 4.75 (s, 4 H), 6.91−7.05 (m, 6 H), 7.27−7.35 (m, 4 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 56.2, 71.1, 74.7, 114.9, 121.8, 129.6, 157.4.

Gold(III)-Catalyzed Standard Organic Reactions (Catalysts: 5 and 7). *1-Bromonaphthalene (**16**),[37] C-1.* Naphthalene (0.780 mmol) and

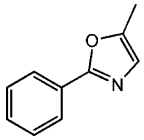


then NBS (0.780 mmol) were added to a solution of catalyst (1 mol %) in CH_2Cl_2 (5 mL). The resulting mixture was stirred for 20 h at 80 °C. No conversion was observed using either IPr or I^{t}Bu catalyst (^{1}H NMR analysis showed only the starting material).

Activated Conditions. Naphthalene (0.780 mmol) and then NBS (0.780 mmol) were added to a solution of catalyst (1 mol %) activated with $AgSbF_6$ (1 mol %) in CH_2Cl_2 (5 mL). The resulting mixture was stirred for 20 h at 80 °C. The mixture was evaporated (no more trace of NBS by ^{1}H NMR) without any workup. Flash column chromatography over silica gel (cyclohexane) gave a mixture of remaining naphthalene and desired product **16**. Yield calculated with internal standard (hexamethylbenzene): $[(IPr)AuCl_2(pyr)](PF_6)$, 56%; $[(I^tBu)AuCl_2(pyr)](PF_6)$, 59%.

^{1}H NMR (300 MHz, $CDCl_3$): 7.33 (t, J = 7.8 Hz, 1 H), 7.62−7.44 (m, 2 H), 7.86−7.75 (m, 3 H), 8.23 (d, J = 8.5 Hz, 1 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 122.8, 126.1, 126.6, 127.0, 127.2, 127.8, 128.2, 129.8, 131.9, 134.6.

*5-Methyl-2-phenyloxazole (**17**),[38] C-2.* *N*-(Prop-2-yn-1-yl)-benzamide (**11**) (0.314 mmol) was added to a solution of catalyst



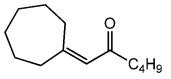
(5 mol %) in CH_2Cl_2 (5 mL). The resulting mixture was stirred at reflux for 20 h. No conversion was observed using either IPr or I^{t}Bu catalyst (^{1}H NMR analysis showed only the starting material).

Activated Conditions. *N*-(Prop-2-yn-1-yl)benzamide (**11**) (0.314 mmol) was added to a solution of catalyst (5 mol %) activated with $AgSbF_6$ (5 mol %) in CH_2Cl_2 (5 mL). The resulting mixture was stirred at reflux (2 h for IPr and overnight for I^{t}Bu). The mixture was evaporated without any workup. Flash column chromatography over silica gel (EA/cyclohexane 30%) gave a mixture of desired methyl-oxazole **17** and methylene-dihydrooxazole **17a** as a colorless oil. $[(IPr)AuCl_2(pyr)](PF_6)$: 38.0 mg, 76% (**17**:**17a**/7:93). $[(I^tBu)AuCl_2(pyr)](PF_6)$: 37.7 mg, 75% (**17**:**17a**/37:63).

*5-Methyl-2-phenyloxazole (**17**).* ^{1}H NMR (300 MHz, $CDCl_3$): 2.40 (d, J = 1.1 Hz, 3 H), 6.84 (q, J = 1.1 Hz, 1 H), 7.39−7.56 (m, 3 H), 7.97−8.02 (m, 2 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 11.1, 124.2, 126.0, 127.8, 128.7, 129.9, 148.9, 160.7.

*5-Methylene-2-phenyl-4,5-dihydrooxazole (**17a**).[59]* ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.37 (q, J = 2.7 Hz, 1 H), 4.66 (t, J = 2.8 Hz, 2 H), 4.82 (q, J = 3.0 Hz, 1 H), 7.39−7.55 (m, 3 H), 7.95−8.01 (m, 2 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): 57.8, 83.8, 126.8, 128.0, 128.5, 131.8, 158.9, 163.8.

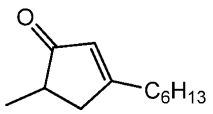
*1-Cycloheptylidenehexan-2-one (**18**),[39] C-3.* A solution of 1-(hex-1-yn-1-yl)cycloheptanol (**12**) (0.309 mmol) in CH_2Cl_2 (2 mL) was



added to a solution of catalyst (5 mol %) in CH_2Cl_2 (3 mL). The resulting mixture was stirred for 20 h at room temperature, then 4 h at reflux. No conversion was observed using either the IPr or I^{t}Bu catalyst (^{1}H NMR analysis showed only the starting material).

Activated Conditions. A solution of 1-(hex-1-yn-1-yl)cycloheptanol (**12**) (0.309 mmol) in CH_2Cl_2 (2 mL) was added to a solution of catalyst (5 mol %) activated with $AgSbF_6$ (5 mol %) in CH_2Cl_2 (3 mL). The resulting mixture was stirred for 1 h at reflux or 20 h at room temperature. No conversion was observed using either the IPr or I^{t}Bu catalyst even under thermal conditions (^{1}H NMR analysis showed only elimination product **18a**: *1-(hex-1-yn-1-yl)cyclohept-1-ene*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.91 (t, J = 7.3 Hz, 3 H), 1.35−2.95 (m, 11 H), 2.11−2.19 (m, 2 H), 2.26−2.34 (m, 3 H), (t, J = 6.7 Hz, 1 H).

*3-Hexyl-5-methylcyclopent-2-enone (**19**),[40] C-4.* A solution of 2-methylundec-1-en-3-yn-5-yl acetate (**13**) (0.270 mmol) in wet CH_2Cl_2

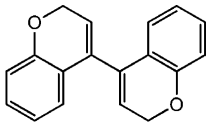


(2 mL) was added to a solution of catalyst (5 mol %) in wet CH_2Cl_2 (3 mL). The resulting mixture was stirred 20 h at room temperature, then 4 h at reflux. No conversion was observed using either IPr or I^{t}Bu catalyst (^{1}H NMR analysis showed only the starting material).

Activated Conditions. A solution of 2-methylundec-1-en-3-yn-5-yl acetate (**13**) (0.270 mmol) in wet CH_2Cl_2 (2 mL) was added to a solution of catalyst (5 mol %) activated with $AgSbF_6$ (5 mol %) in wet CH_2Cl_2 (3 mL). The resulting mixture was stirred for 1.5 h at reflux. The mixture was evaporated without any workup. Flash column chromatography over silica gel (EA/cyclohexane 5%) gave the desired product **19** as a yellowish oil. $[(IPr)AuCl_2(pyr)](PF_6)$: 39.6 mg, 81%. $[(I^tBu)AuCl_2(pyr)](PF_6)$: 33.8 mg, 70%.

^{1}H NMR (300 MHz, $CDCl_3$): 0.89 (t, J = 6.9 Hz, 3 H), 1.15 (d, J = 7.5 Hz, 3 H), 1.26−1.38 (m, 6 H), 1.52−1.62 (m, 2 H), 2.16 (d, J_{AB} = 18.3 Hz, 1 H), 2.83 (t, J = 7.7 Hz, 2 H), 2.36−2.45 (m, 1 H), 2.81 (dd, J_{AB} = 18.3 Hz, J = 6.7 Hz, 1 H), 5.90 (s, 1 H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): 14.0, 16.5, 22.5, 27.0, 29.0, 31.6, 33.5, 40.4, 40.7, 128.2, 181.4, 212.7.

*2H,2′H-4,4′-Bichromene (**20**),[41] C-5.* 1,6-Diphenoxyhexa-2,4-diyne (**15**) (0.381 mmol) was added to a solution of catalyst (5 mol %) in



CH_2Cl_2 (5 mL). The resulting mixture was stirred for 20 h at room temperature, then 4 h at reflux. No conversion was observed using

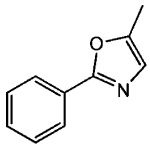
dx.doi.org/10.1021/om400338k | *Organometallics* 2013, 32, 4153−4164

either IPr or I^{t}Bu catalyst (^{1}H NMR analysis showed only the starting material).

Activated Conditions. 1,6-Diphenoxyhexa-2,4-diyne (**15**) (0.381 mmol) was added to a solution of catalyst (5 mol %) activated with $AgSbF_6$ (5 mol %) in CH_2Cl_2 (5 mL). The resulting mixture was stirred for 4 h at reflux. The mixture was evaporated without any workup. Flash column chromatography over silica gel (EA/cyclohexane 5%) gave the desired product (**20**) as a yellow solid. [(IPr)$AuCl_2$(pyr)](PF_6): 69.7 mg, 70%. [(I^{t}Bu)$AuCl_2$(pyr)](PF_6): 68.7 mg, 69%.

^{1}H NMR (300 MHz, $CDCl_3$): 4.89 (d, J = 3.8 Hz, 2 H), 5.83 (t, J = 3.8 Hz, 1 H), 6.77 (td, J = 7.5, 1.2 Hz, 1 H), 6.86 (dd, J = 8.1, 1.2 Hz, 1 H), 6.89 (dd, J = 7.5, 1.7 Hz, 1 H), 7.11 (ddd, J = 8.1, 7.5, 1.7 Hz, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 65.4, 116.2, 121.5, 122.9, 125.9, 129.5, 134.0, 154.1.

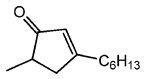
Gold(I)-Catalyzed Standard Organic Reactions (catalyst: 1). *5-Methyl-2-phenyloxazole (17),*[38] *C-2. Activated Conditions.*



N-(Prop-2-yn-1-yl)benzamide (**11**) (0.314 mmol) was added to a solution of catalyst (5 mol %) activated with $AgSbF_6$ (5 mol %) in CH_2Cl_2 (5 mL). The resulting mixture was stirred at reflux for 2.5 h. The mixture was evaporated without any workup. Flash column chromatography over silica gel (EA/cyclohexane 30%) gave a mixture of the desired methyl-oxazole **17** and methylene-dihydrooxazole **17a** as a colorless oil in 56% yield.

C-2. Nonactivated Conditions. *N*-(Prop-2-yn-1-yl)benzamide (**11**) (0.314 mmol) was added to a solution of catalyst (5 mol %) in CH_2Cl_2 (5 mL). The resulting mixture was stirred at reflux for 4 h. The mixture was evaporated without any workup. Flash column chromatography over silica gel (EA/cyclohexane 30%) gave a mixture of the desired methyl-oxazole **17** and methylene dihydrooxazole **17a** as a colorless oil in 77% yield.

3-Hexyl-5-methylcyclopent-2-enone (19),[40] *C-4. Activated Conditions.* A solution of 2-methylundec-1-en-3-yn-5-yl acetate (**13**)



(0.270 mmol) in wet CH_2Cl_2 (2 mL) was added to a solution of catalyst (5 mol %) activated with $AgSbF_6$ (5 mol %) in wet CH_2Cl_2 (3 mL). The resulting mixture was stirred for 4.5 h at room temperature. The mixture was evaporated without any workup. Flash column chromatography over silica gel (EA/cyclohexane 5%) gave the desired product **19** as a yellowish oil in 65% yield.

C-4. Nonactivated Conditions. A solution of 2-methylundec-1-en-3-yn-5-yl acetate (**13**) (0.270 mmol) in wet CH_2Cl_2 (2 mL) was added to a solution of catalyst (5 mol %) in wet CH_2Cl_2 (3 mL). The resulting mixture was stirred for 4.5 h at reflux. Flash column chromatography over silica gel (EA/cyclohexane 5%) gave the desired product **19** as a yellowish oil in 72% yield.

■ ASSOCIATED CONTENT

Supporting Information

The NMR and crystal data of **2**–**9** are available. The crystallographic information files (CIF) have been deposited with the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K., and can be obtained on request, free of charge, by quoting the publication citation and deposition numbers 929408–929412 and 929414–929416. This material is also available free of charge via the Internet at http://pubs.acs.org. The NMR studies for the attempted synthesis of [(PPh_3)$AuCl_2$(Pyr)](PF_6) are also presented.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The Centre National de la Recherche Scientifique (CNRS) and the Ministère de la Recherche are gratefully acknowledged for financial support of this work. Johnson Matthey PLC is also gratefully acknowledged for a generous loan of gold metal. A.B. and D.H. thank the Agence Nationale de la Recherche (ANR) for financial support and a Ph.D. fellowship (Grant ANR-11-JS07-001-01 Synt-Het-Au). S.O. thanks Prof. Claudio Pettinari and Prof. Fabio Marchetti for encouraging and financially supporting her Ph.D. mobility between the University of Camerino and the University of Strasbourg.

■ REFERENCES

(1) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

(2) Common NHC-transition metal complexes used as catalysts: (a) [Ru/metathesis]: Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746–1787 and references therein. (b) [Pd/coupling]: Würtz, S.; Glorius, F. *Acc. Chem. Res.* **2008**, *41*, 1523–1533. (c) Bellina, F.; Rossi, R. *Chem. Rev.* **2010**, *110*, 1082–1146 and references therein. (d) [Rh/Ir]: Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612–3676 and references therein. (e) Gil, W.; Trzeciak, A. M. *Coord. Chem. Rev.* **2011**, *255*, 473–483 and references therein.

(3) Lin, J. C. Y.; Huang, R. T. W.; Lee, C. S.; Bhattacharrya, A.; Hwang, W. S.; Lin, I. J. B. *Chem. Rev.* **2009**, *109*, 3561–3598.

(4) (a) de Frémont, P.; Stevens, E. D.; Fructos, M. R.; Díaz-Requejo, M. M.; Pérez, P. J.; Nolan, S. P. *Chem. Commun.* **2006**, 2045–2047. (b) de Frémont, P.; Marion, N.; Nolan, S. P. *J. Organomet. Chem.* **2009**, *694*, 551–560. (c) Ramón, R. S.; Gaillard, S.; Poater, A.; Cavallo, L.; Slawin, A. M. Z.; Nolan, S. P. *Chem.—Eur. J.* **2011**, *17*, 1238–1246.

(5) Zuccaccia, D.; Belpassi, L.; Tarantelli, F.; Macchioni, A. *J. Am. Chem. Soc.* **2009**, *131*, 3170–3171.

(6) (a) Brown, T. J.; Widenhoefer, R. A. *J. Organomet. Chem.* **2011**, *696*, 1216–1220. (b) Brown, T. J.; Widenhoefer, R. A. *Organometallics* **2011**, *30*, 6003–6009.

(7) Brown, T. J.; Sugie, A.; Leed, M. G. D.; Widenhoefer, R. A. *Chem.—Eur. J.* **2012**, *18*, 6959–6971.

(8) de Frémont, P.; Clavier, H.; Rosa, V.; Avilés, T.; Braunstein, P. *Organometallics* **2011**, *30*, 2241–2251.

(9) (a) Dash, C.; Kroll, P.; Yousufuddin, M.; Dias Rasika, H. V. *Chem. Commun.* **2011**, *47*, 4478–4480. (b) Celik, M. A.; Dash, C.; Adiraju, V. A. K.; Das, A.; Yousufuddin, M.; Frenking, G.; Rasika Dias, H. V. *Inorg. Chem.* **2013**, *52*, 729–742.

(10) Kinjo, R.; Donnadieu, B.; Bertrand, G. *Angew. Chem. Int. Ed.* **2011**, *50*, 5560–5563.

(11) Weber, S. G.; Rominger, F.; Straub, B. F. *Eur. J. Inorg. Chem.* **2012**, 2863–2867.

(12) Laitar, D. S.; Müller, P.; Gray, T. G.; Sadighi, J. P. *Organometallics* **2005**, *24*, 4503–4505.

(13) (a) Gaillard, S.; Slawin, A. M. Z.; Nolan, S. P. *Chem. Commun.* **2010**, *46*, 2742–2744. (b) Gómez-Súarez, A.; Ramón, R. S.; Slawin, A. M. Z.; Nolan, S. P. *Dalton Trans.* **2012**, *41*, 5461–5463.

(14) Tsui, E. Y.; Müller, P.; Sadighi, J. P. *Angew. Chem. Int. Ed.* **2008**, *47*, 8937–8940.

(15) (a) Ricard, L.; Gagosz, F. *Organometallics* **2007**, *26*, 4704–4707. (b) Gómez-Súarez, A.; Ramón, R. S.; Songis, O.; Slawin, A. M. Z.; Cazin, C. S. J.; Nolan, S. P. *Organometallics* **2011**, *30*, 5463–5470.

(16) Zhang, C.-P.; Vicic, D. A. *Organometallics* **2012**, *31*, 7812–7815.

(17) (a) Gómez-Suárez, A.; Dupuy, S.; Slawin, A. M. Z.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2013**, *52*, 938–942. (b) Hashmi, A. S. K.; Lauterbach, T.; Nösel, P.; Vilhelmsen, M. H.; Rudolph, M.; Rominger, F. *Chem.—Eur. J.* **2013**, *19*, 1058–1065.

(18) (a) Hoffmann, R. *Angew. Chem., Int. Ed.* **1982**, *21*, 711−724. (b) Mingos, D. M. P. *Gold Bull.* **1984**, *17*, 5−12. (c) Braunstein, P.; Rosé, J. *Gold Bull.* **1985**, *18*, 17−30. (d) Parish, R. V. *Gold Bull.* **1997**, *30*, 3−12. (e) Schmidbaur, H. *Gold Bull.* **1999**, *33*, 3−10. (f) Sculfort, S.; Braunstein, P. *Chem. Soc. Rev.* **2011**, *40*, 2741−2760.
(19) Robilotto, T. J.; Bacsa, J.; Gray, T. G.; Sadighi, J. P. *Angew. Chem., Int. Ed.* **2012**, *51*, 12077−12080.
(20) (a) de Frémont, P.; Singh, R.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2007**, *26*, 1376−1385. (b) Gaillard, S.; Bantreil, X.; Slawin, A. M. Z.; Nolan, S. P. *Dalton Trans.* **2009**, 6967−6971. (c) Boronat, M.; Corma, A.; González-Arellano, C.; Iglesias, M.; Sánchez, F. *Organometallics* **2010**, *29*, 134−141. (d) Baron, M.; Tubaro, C.; Basato, M.; Biffis, A.; Natile, M. M.; Graiff, C. *Organometallics* **2011**, *30*, 4607−4615. (e) Hirtenlehmer, C.; Krims, C.; Hölbling, J.; List, M.; Zabel, M.; Fleck, M.; Berger, R. J. F.; Schoefberger, W.; Monkowius, U. *Dalton Trans.* **2011**, *40*, 9899−9910.
(21) Mankad, N. P.; Toste, F. D. *J. Am. Chem. Soc.* **2010**, *132*, 12859−12861.
(22) (a) Au, V. K.-M.; Wong, K. M.-C.; Zhu, N.; Yam, V. W.-W. *J. Am. Chem. Soc.* **2009**, *131*, 9076−9085. (b) Bronner, C.; Wenger, O. S. *Dalton Trans.* **2011**, *40*, 12409−12420. (c) To, W.-P.; Tong, G. S.-M.; Lu, W.; Ma, C.; Liu, J.; Chow, A. L.-F.; Che, C.-M. *Angew. Chem., Int. Ed.* **2012**, *51*, 2654−2657.
(23) Jacques, B.; Kirsch, J.; de Frémont, P.; Braunstein, P. *Organometallics* **2012**, *31*, 4654−4657.
(24) Topf, C.; Hirtenlehner, C.; Fleck, M.; List, M.; Monkowius, U. *Z. Anorg. Allg. Chem.* **2011**, *637*, 2129−2134.
(25) Topf, C.; Hirtenlehner, C.; Zabel, M.; List, M.; Fleck, M.; Monkowius, U. *Organometallics* **2011**, *30*, 2755−2764.
(26) Wimberg, J.; Meyer, S.; Dechert, S.; Meyer, F. *Organometallics* **2012**, *31*, 5025−5033.
(27) (a) Pažický, M.; Loos, A.; Ferreira, M. J.; Serra, D.; Vinokurov, N.; Rominger, F.; Jäkel, C.; Hashmi, A. S. K.; Limbach, M. *Organometallics* **2010**, *29*, 4448−4458. (b) Tomás-Mendivil, E.; Toullec, P. Y.; Díez, J.; Conejero, S.; Michelet, V.; Cadierno, V. *Org. Lett.* **2012**, *14*, 2520−2523. (c) Muuronen, M.; Perea-Buceta, J. E.; Nieger, M.; Patzschke, M.; Helaja, J. *Organometallics* **2012**, *31*, 4320−4330.
(28) Recent reviews on homogeneous gold catalysis: (a) Marion, N.; Nolan, S. P. *Chem. Soc. Rev.* **2008**, *37*, 1776−1782. (b) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2010**, *49*, 5232−5241. (c) Nolan, S. P. *Acc. Chem. Res.* **2011**, *44*, 91−100. (d) Rudolph, M.; Hashmi, S. K. *Chem. Soc. Rev.* **2012**, *41*, 2448−2462. (e) Corma, A.; Leyva-Pérez, A.; Sabater, M. J. *Chem. Rev.* **2011**, *111*, 1657−1712. (f) Leyva-Pérez, A.; Corma, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 614−635.
(29) (a) Hindi, K. M.; Panzner, M. J.; Tessier, C. A.; Cannon, C. L.; Youngs, W. J. *Chem. Rev.* **2009**, *109*, 3859−3884 and references therein. (b) Yan, J. J.; Chow, A. L.-F.; Leung, C.-H.; Sun, R. W.-Y.; Ma, D.-L.; Che, C.-M. *Chem. Commun.* **2010**, *46*, 3893−3895. (c) Weaver, J.; Gaillard, S.; Toye, C.; Macpherson, S.; Nolan, S. P.; Riches, A. *Chem.—Eur. J.* **2011**, *17*, 6620−6624. (d) Siravam, H.; Tan, J.; Huynh, H. V. *Organometallics* **2012**, *31*, 5875−5883.
(30) (a) Zhang, G.; Peng, Y.; Cui, L.; Zhang, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 3112−3115. (b) Hopkinson, M. N.; Tessier, A.; Salisbury, A.; Giuffredi, G. T.; Combettes, L. E.; Gee, A. D.; Gouverneur, V. *Chem.—Eur. J.* **2010**, *16*, 4739−4743. (c) Brenzovich, W. E.; Benitez, D., Jr.; Lackner, A. D.; Shunatona, H. P.; Tkatchouk, E.; Goddard, W. A., III; Toste, F. D. *Angew. Chem., Int. Ed.* **2010**, *49*, 5519−5522. (d) Zhang, G.; Luo, Y.; Wang, Y.; Zhang, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 4450−4454. (e) Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A. *Chem.—Eur. J.* **2012**, *18*, 2931−2937.
(31) (a) Bartolomé, C.; Ramiro, Z.; Garciá-Cuadrado, D.; Pérez-Galán, P.; Raducan, M.; Bour, C.; Echavarren, A. M.; Espinet, P. *Organometallics* **2010**, *29*, 951−956. (b) Wang, G.; Zou, Y.; Li, Z.; Wang, Q.; Goeke, A. *J. Org. Chem.* **2011**, *76*, 5825−5831. (c) Marinetti, A.; Jullien, H.; Voituriez, A. *Chem. Soc. Rev.* **2012**, *41*, 4884−4908 and references therein. (d) Yamada, K.-i.; Matsumoto, Y.; Selim, K. B.; Yamamoto, Y.; Tomioka, K. *Tetrahedron* **2012**, *68*, 4159−4165.
(32) Krause, N.; Winter, C. *Chem. Rev.* **2011**, *111*, 1994−2009 and references therein.
(33) (a) Melhado, A. D.; Brenzovich, W. E., Jr.; Lackner, A. D.; Toste, F. D. *J. Am. Chem. Soc.* **2010**, *132*, 8885−8887. (b) Ball, L. T.; Green, M.; Lloyd-Jones, G. C.; Russell, C. A. *Org. Lett.* **2010**, *12*, 4724−4727. (c) Ball, L. T.; Green, M.; Lloyd-Jones, G. C.; Russell, C. A. *Chem.—Eur. J.* **2012**, *18*, 2931−2937.
(34) (a) Jean, M.; van de Weghe, P. *Tetrahedron Lett.* **2011**, *52*, 3509−3513. (b) Peshkov, V. A.; Pereshivko, O. P.; Van der Eycken, E. V. *Adv. Synth. Catal.* **2012**, *354*, 2841−2848.
(35) (a) Bender, C. F.; Widenhoefer, R. A. *Chem. Commun.* **2008**, 2741−2743. (b) Dash, C.; Shaikh, M. M.; Butcher, R. J.; Ghosh, P. *Inorg. Chem.* **2010**, *49*, 4972−4983. (c) Hesp, K. D.; Stradiotto, M. *J. Am. Chem. Soc.* **2010**, *132*, 18026−18029. (d) Butler, K. L.; Tragni, M.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 5175−5178.
(36) (a) Vidadala, S. R.; Gayatri, G.; Sastry, G. N.; Hotha, S. *Chem. Commun.* **2011**, *47*, 9906−9908. (b) Yu, J.; Sun, J.; Yu, B. *Org. Lett.* **2012**, *14*, 4022−4025. (c) Yang, F.; Wang, Q.; Yu, B. *Tetrahedron. Lett.* **2012**, *53*, 5231−5234.
(37) Mo, F.; Yan, J. M.; Qiu, D.; Li, F.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 2028−2032.
(38) Hashmi, A. S. K.; Weyrauch, J. P.; Frey, W.; Bats, J. W. *Org. Lett.* **2004**, *6*, 4391−4394.
(39) Pennell, M. N.; Turner, P. G.; Sheppard, T. D. *Chem.—Eur. J.* **2012**, *18*, 4748−4758.
(40) Zhang, L.; Wang, S. *J. Am. Chem. Soc.* **2006**, *128*, 1442−1443.
(41) Mo, J.; Eom, D.; Lee, E.; Lee, P. H. *Org. Lett.* **2012**, *14*, 3684−3687.
(42) (a) de Frémont, P.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 2411−2418. (b) Hashmi, A. S. K.; Yu, Y.; Rominger, F. *Organometallics* **2012**, *31*, 895−904. (c) Sato, T.; Hirose, Y.; Yoshioka, D.; Oi, S. *Organometallics* **2012**, *31*, 6995−7003. (d) Xu, X.; Kim, S. H.; Zhang, X.; Das, A. K.; Hirao, H.; Hong, S. H. *Organometallics* **2013**, *32*, 164−171.
(43) (a) Thwaite, S. E.; Schier, A.; Schmidbaur, H. *Inorg. Chim. Acta* **2004**, *357*, 1549−1557. (b) Mullice, L. A.; Thorp-Greenwood, F. L.; Laye, R. H.; Coogan, M. P.; Kariuki, B. M.; Pope, S. J. A. *Dalton Trans.* **2009**, 6836−6842. (c) Chiou, J. Y. Z.; Luo, S. C.; You, W. C.; Bhattacharyya, A.; Vasam, C. S.; Huang, C. H.; Lin, I. J. B. *Eur. J. Inorg. Chem.* **2009**, 1950−1959.
(44) Braunstein, P.; Clark, R. J. H. *Inorg. Chem.* **1974**, *13*, 2224−2229.
(45) (a) Bourosh, P.; Bologa, O.; Simonov, Y.; Gerbeleu, N.; Lipkowski, J.; Gdaniec, M. *Inorg. Chim. Acta* **2007**, *360*, 3250−3254. (b) Cinellu, M. A.; Cocco, F.; Minghetti, G.; Stoccoro, S.; Zucca, A.; Manassero, M. *J. Organomet. Chem.* **2009**, *694*, 2949−2955.
(46) Gaillard, S.; Slawin, A. M. Z.; Bonura, A. T.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2010**, *29*, 394−402.
(47) $IPrAuCl_3$-CH_2Cl_2: CSD refcode: EJANAF; cell: a = 10.55 Å, b = 16.41 Å, c = 19.07 Å, α = 91.65°, β = 105.99°, γ = 107.01°, $P\bar{1}$; polymorph: $IPrAuCl_3$:; cif deposition number: 929413; cell: a = 18.83 Å, b = 12.59 Å, c = 24.23 Å, α = 90°, β = 92.76°, γ = 90°, $P2_1/c$.
(48) Chen, C. Y.; Zeng, J. Y.; Lee, H. M. *Inorg. Chim. Acta* **2007**, *360*, 21−30.
(49) Pazderski, L.; Toušek, J.; Sitkowski, J.; Kozerski, L.; Marek, R.; Szłyk, E. *Magn. Reson. Chem.* **2007**, *45*, 24−36.
(50) (a) Baenziger, N. C.; Dittemore, K. M.; Doyle, J. R. *Inorg. Chem.* **1974**, *13*, 805−811. (b) Vollenbroek, F. A.; van den Berg, J. P.; van der Velden, J. W. A.; Bour, J. J. *Inorg. Chem.* **1980**, *19*, 2685−2688. (c) King, C.; Khan, M. N. I.; Staples, R.; Fackler, J. P., Jr. *Inorg. Chem.* **1992**, *31*, 3236−3238. (d) Staples, R. J.; King, C.; Khan, M. N. I.; Winpenny, R. E. P.; Fackler, J. P., Jr. *Acta Crystallogr.* **1993**, *C49*, 472−475.
(51) The IR spectra of the decomposition products are too crowded to be conclusive for the formation of PPh_3=O. Reference IR database: http://sdbs.riodb.aist.go.jp/sdbs/cgi-bin/direct_frame_top.cgi.
(52) Serafimova, I. M.; Hoggard, P. E. *Inorg. Chim. Acta* **2002**, *338*, 105−110.

(53) Adams, H.-N.; Strähle, J. *Z. Anorg. Allg. Chem.* **1982**, *485*, 65−80.
(54) (a) Schneider, D.; Schier, A.; Schmidbaur, H. *Dalton Trans.* **2004**, 1995−2005. (b) Schneider, D.; Schuster, O.; Schmidbaur, H. *Dalton Trans.* **2005**, 1940−1947.
(55) Wang, D.; Cai, R.; Sharma, S.; Jirak, J.; Thummanapelli, S. K.; Akhmedov, N. G.; Zhang, H.; Liu, X.; Petersen, J. L.; Shi, X. *J. Am. Chem. Soc.* **2012**, *134*, 9012−9019.
(56) Sheldrick, G. M. *Acta Crystallogr.* **1997**, *A64*, 112−122.
(57) Kalyani, D.; Sanford, M. S. *J. Am. Chem. Soc.* **2008**, *130*, 2150−2151.
(58) Cordonnier, M. C.; Blanc, A.; Pale, P. *Org. Lett.* **2008**, *10*, 1569−1572.
(59) Meng, X.; Kim, S. *Org. Biomol. Chem.* **2011**, *9*, 4429−4431.