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Markovnikov at Gold: Nucleophilic Addition to Alkenes at Au(III)

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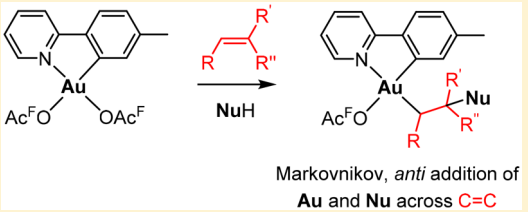
Supporting Information

ABSTRACT: The reactivity of $Au(OAc^F)_2(tpy)$ (**1**, OAc^F = $OCOCF_3$; tpy = 2-(*p*-tolyl)pyridine) toward a wide variety of different alkenes with varying substitution patterns and different oxygen-based nucleophiles has been investigated. These reactions are two-step processes where a ligand substitution is followed by a nucleophilic addition furnishing Au(III) complexes with C(sp^3) ligands. In this work we have found that the reactions always occur *trans* to tpy-*N* while the OAc^F ligand remains in place *trans* to tpy-C. The nucleophilic addition takes place exclusively at the most substituted side of the double bond, in a Markovnikov manner, and the nucleophilic addition occurs in an *anti* fashion as can be seen from the reaction with the 2,3-disubstituted alkene *trans*-2-hexene. This study has provided valuable insight into the scope and regiochemistry of Au(III) mediated nucleophilic additions, which is of great importance for further development of Au(III) catalysis and alkene functionalization.



INTRODUCTION

The interest in gold and its rich chemistry has increased rapidly the last 20−30 years.[1−9] Gold is known for its ability to activate alkenes and alkynes toward nucleophilic attack and addition of nucleophiles to coordinated unsaturated species at gold are key steps in gold catalysis.[1−12] Functionalization of alkenes and alkynes under mild conditions is of great interest because readily available hydrocarbon building blocks can be converted into useful compounds. Catalytic Au functionalization of heavily functionalized, unsaturated precursors into complex organic structures has been widely investigated.[2,4−6] The more simple precursors, such as ethylene and other small alkenes, have however received less attention.

There are only a few examples of ethylene functionalization at Au(III) in the literature. Atwood and co-workers reported that ethylene could be stoichiometrically functionalized at $[Au(bipy)Cl_2]^+$ (bipy = 2,2′-bipyridine) to furnish Au(III) hydroxyalkyl complexes that were observed in solution by ^{1}H NMR but not isolated.[13] Bochmann and co-workers reported that ethylene undergoes a slow formal insertion into the Au-OAc^F (OAc^F = $OCOCF_3$) bond in a diarylpyridine CNC pincer complex.[14] Bourissou and co-workers recently reported coordination−insertion reactions of norbornene[15−17] and ethylene,[17,18] the latter followed by *β*-hydride elimination, into Au−C(sp^3) and Au−C(sp^2) bonds in (P,C)-cyclometalated Au(III) aryl and alkyl complexes. Following this, the same group very recently reported a double insertion of ethylene into an Au−C(sp^2) bond in a (N,C) cyclometalated Au(III) complex; in this case no *β*-hydride elimination occurred.[19] Recently Russell, Bower and co-workers reported an oxidative 1,2-difunctionalization of ethylene via gold catalysis where one of the proposed key steps involves addition of an alcohol to ethylene at Au(III).[20]

We previously reported a detailed mechanistic study combining experiments and DFT calculations of the formal insertion of ethylene into the Au−O bond *trans* to tpy-*N* in $Au(OAc^F)_2(tpy)$ (**1**, tpy = 2-(*p*-tolyl)pyridine) furnishing **2** (Scheme 1, top).[21] When the reaction was performed in CF_3CH_2OH **3** was formed instead of **2**.[21] These reactions are two-step processes where a ligand substitution is followed by a nucleophilic addition to the double bond to furnish a Au−C(sp^3) bonded complex. In contrast to the formal insertion process, the coordination−insertion process reported by Bourissou and co-workers is a one-step concerted process.[15−18]

In order to gain further insight into the scope and regiochemistry of the reaction, substituted alkenes and different oxygen based nucleophiles were investigated. Herein we report the Au(III) mediated nucleophilic addition to a wide variety of alkenes (Scheme 1, bottom) at **1**, furnishing a wide range of Au(III) complexes with C(sp^3) bonded ligands.

RESULTS AND DISCUSSION

Substituted Alkenes with $^-OAc^F$ as Nucleophile. The reaction of **1** with 1-hexene provides two different positions at which the nucleophilic addition can occur (Scheme 2), either at the internal position of the double bond leading to **4a** (in a Markovnikov manner) or at the terminal position of the double bond leading to **4a′**. When monitoring the reaction of **1** with 1-hexene in $DOAc^F$ by ^{1}H NMR, a clean transformation of **1** into one product, **4a** (vide infra), was observed within minutes. It

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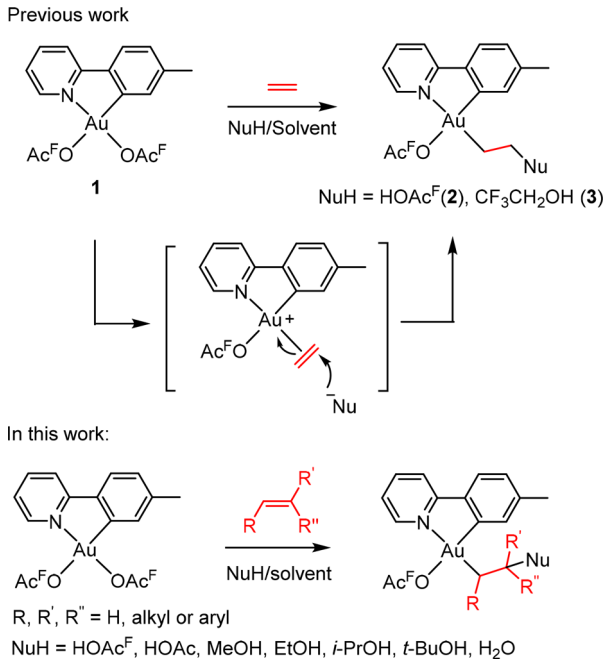
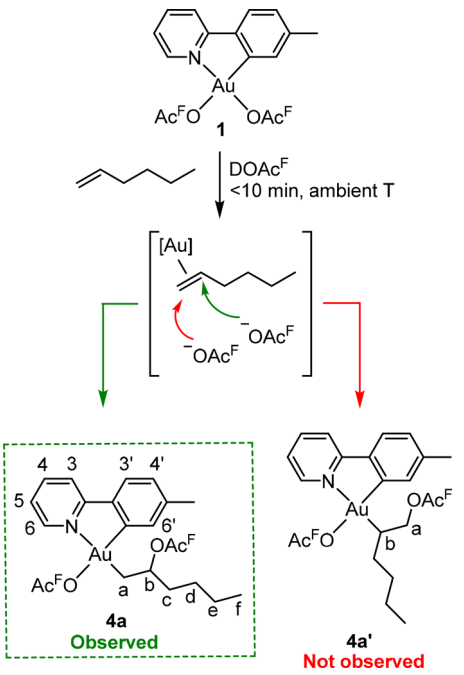
Scheme 1. Top: Formal Insertion of Ethylene into the Au−O Bond *trans* to tpy-*N* in $Au(OAc^F)_2(tpy)$ (1, OAc^F = $OCOCF_3$; tpy = 2-(*p*-tolyl)pyridine) Furnishing 2 and 3;[21] Bottom: Reactivity of $Au(OAc^F)_2(tpy)$ toward a Range of Alkenes and Nucleophiles Furnishing *β*-Functionalized Alkyl Complexes of Au(III)



Scheme 2. Formal Insertion of 1-Hexene into the Au−O Bond *trans* to tpy-*N* in a Markovnikov Manner Furnishing 4a[a]



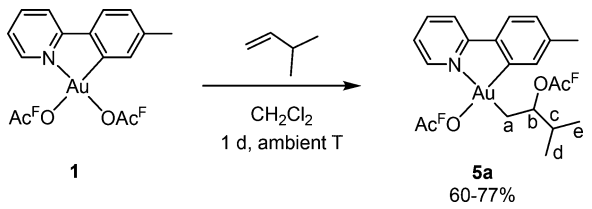
[a]Complex **4a′** was not observed. [Au] = $[Au(tpy)(OAc^F)]^+$. The atoms in the former 1-hexene unit are here labeled a−f to simplify the NMR discussions.

was not possible to isolate **4a** from the $DOAc^F$ solution because it decomposes upon removal of the solvent. Complex **4a** could however be characterized in a mixture of CD_2Cl_2 and $HOAc^F$ (ca. 2 vol % $HOAc^F$ in CD_2Cl_2) by standard NMR techniques.

The ^1H NMR spectrum of **4a** in CD_2Cl_2 exhibits some characteristic resonances; at δ 5.40 a resonance with a complex splitting pattern originating from H^b (see numbering, Scheme 2) is observed which indicates the formation of **4a** and not **4a′** (in the case of **4a′** H^b would be expected at a lower ppm value). Furthermore, at δ 2.42 and ca. δ 2.5 the resonances of the two diastereotopic H^a (the latter overlapping with tpy-CH_3) are observed ($^2J_{HH}$ = 10.4 Hz), again indicating the formation of **4a** and not **4a′**, since in **4a′** these two diastereotopic protons would be expected at significantly higher ppm values. At δ 1.94 H^c is observed, at δ 1.20−1.50 the overlapping resonances of H^d and H^e are observed, and finally, at δ 0.91 a triplet belonging to the methyl group at the end of the alkyl chain is observed. The ^{19}F NMR of a sample of **4a** gave two resonances at δ −77.1 and −78.0, similar to the chemical shifts observed for **2** and corresponding to the two OAc^F groups. A $^{19}F-^1H$ HOESY experiment (see SI) established that the resonance at δ −77.1 arises from the OAc^F ligand *trans* to tpy-C. As in the reaction of **1** with ethylene (Scheme 1), the insertion occurred in the position *trans* to tpy-*N* as could be seen from a NOESY experiment (see SI) where a NOE was observed between H^a and $H^{6'}$, and between H^b and $H^{6'}$ (for atom numbering, see Scheme 2).

Nucleophilic addition to the more sterically crowded alkene 3-methyl-1-butene could also be achieved (Scheme 3). Upon

Scheme 3. Formal Insertion of 3-Methyl-1-butene into the Au−O Bond *trans* to tpy-*N* in 1[a]



[a]The atoms in the former 3-methyl-1-butene unit are here labeled a−e to simplify the NMR discussions.

reacting **1** with 3-methyl-1-butene in CH_2Cl_2 complex **5a** was formed. **5a** was significantly more stable than **4a** and could easily be isolated in 60−77% yield. **5a** was characterized by NMR, MS, X-ray crystallography (as a $CHCl_3$ solvate, vide infra), and elemental analysis. Also in this reaction, nucleophilic addition occurred at the internal position of the alkene. In the ^1H NMR spectrum of **5a** H^b is found at δ 5.31, similar to **4a** where H^b is found at δ 5.40. The two diastereotopic H^a are found at δ 2.60 and δ 2.32 ($^2J_{HH}$ = 10.7 Hz). H^c is found at δ 2.21 and the two diastereotopic methyl groups ($CH_3{}^d$ and $CH_3{}^e$) are found at δ 1.07 and δ 1.05. In the ^{19}F NMR of **5a** two resonances at δ −77.0 and −77.9, similar to **4a** and corresponding to the two OAc^F ligands, were observed. In the ^{13}C NMR of **5a** two sets of two quartets corresponding to the carbons in the two OAc^F ligands were observed at δ 161.3, 157.6, 118.2, and 115.0, with $J_{19F-13C}$ = 37.3, 41.6, 290.1, and 286.4 Hz, respectively. As in **4a**, a NOESY experiment established that the reaction had occurred in the position *trans* to tpy-*N* (see SI), where a NOE was observed between H^a and $H^{6'}$, and between H^b and $H^{6'}$ (for numbering, see Scheme 2).

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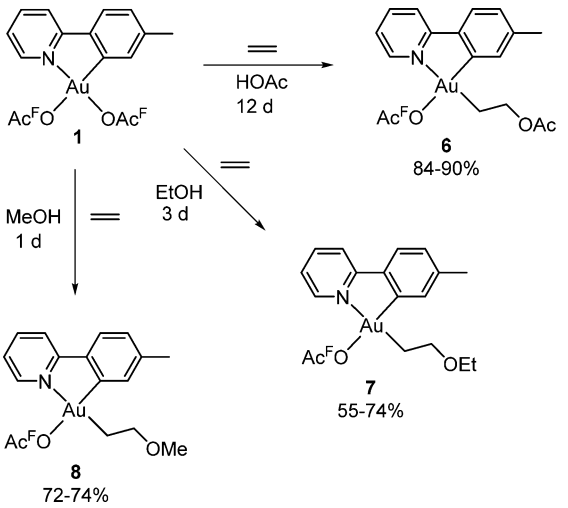
The disubstituted and trisubstituted alkenes 2-methyl-1-butene and 2-methyl-2-butene were also investigated under the same reaction conditions as for **5a**, however no insertion products could be isolated.

Ethylene with Other Nucleophiles. The formal insertions performed in $HOAc^F$ showed a limited scope and gave products of variable stability. To extend the scope of these reactions, it was desired to investigate other nucleophiles. Acetic acid (HOAc) and ethanol were investigated in the ethylene reaction (Scheme 1, top) and it turned out that upon simply bubbling ethylene through a mixture of **1** in HOAc or ethanol followed by stirring at ambient temperature, the corresponding acetate and ethoxy products **6** and **7** (Scheme 4)

Scheme 4. Au(III) Mediated Nucleophilic Addition of HOAc, MeOH, and EtOH to Ethylene Furnishing 6, 7, and 8[a]



[a]All the reactions depicted in this scheme were performed at ambient temperature.

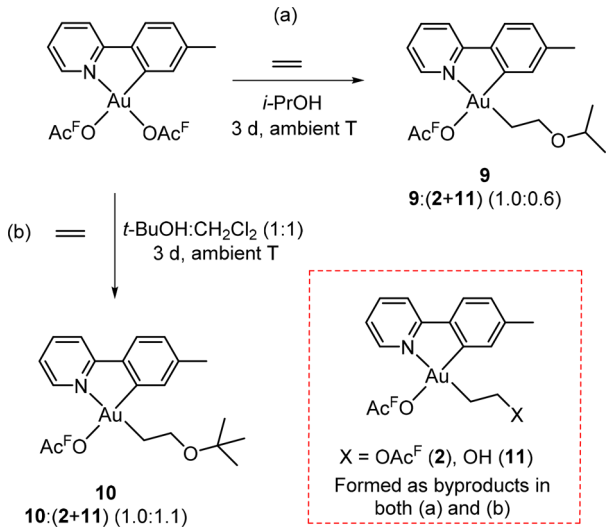
could be obtained. The reaction in HOAc was rather slow and 12 days were needed in order to obtain full conversion into product. The reaction in ethanol was faster but in this case byproduct formation complicated the reaction (see SI for details). Methanol was also tested as a nucleophile, and upon bubbling ethylene through a mixture of **1** in methanol **8** could easily be obtained in a good yield (Scheme 4).

Complexes **6** and **8** were characterized by NMR, MS, X-ray diffraction analysis (vide infra), and elemental analysis. Complex **7** was characterized by NMR and MS. All complexes **6**, **7**, and **8** contain the characteristic resonances for the CH_2CH_2 moiety originating from ethylene in the ^1H NMR spectrum at δ 4.42 and δ 2.38 for **6**, at δ 3.74 and δ 2.40 for **7**, and at δ 3.68 and δ 2.39 for **8**. In the ^1H NMR spectrum of **6** the resonance corresponding to the acetate group is observed at δ 2.04, in **7** a quartet and a triplet corresponding to the OEt group are seen at δ 3.55 and δ 1.19, respectively, and the resonance corresponding to the methoxy group of **8** is observed at δ 3.38. A NOE correlation between the CH_2CH_2 protons and $H^{6'}$ (see Scheme 2 for numbering) was observed for all three complexes, indicating that the reactions had all occurred *trans* to tpy-*N*.

When investigating the complexes by ^{19}F NMR it became evident that the OAc^F group *trans* to tpy-*C* has remained in all of the three complexes. No exchange of the OAc^F group *trans* to tpy-*C* with either OAc, OMe, or OEt could be observed. For all three complexes, a single resonance at δ −77.0 in the ^{19}F NMR spectra and a set of two quartets in the ^{13}C NMR spectra could be observed, corresponding to the OAc^F group *trans* to tpy-*C*.

The more sterically crowded nucleophiles, *i*-PrOH and *t*-BuOH were also investigated (Scheme 5). In this case,

Scheme 5. Au(III) Mediated Nucleophilic Addition of *i*-PrOH and *t*-BuOH to Ethylene Furnishing 9 and 10[a]



[a]Complexes **2** and **11** were formed as byproducts in both reactions.

competition from the OAc^F ligand that has to dissociate from **1** was observed, leading to formation of the previously reported complex **2**[21] together with **9** and **10**. Furthermore, another byproduct, which is assigned to be complex **11** (see SI for details), was observed. Complex **11** may originate from addition of water to ethylene at Au. Despite repeated efforts to exclude water from the reaction 11 was always formed. Small amounts of **11** (<15%) were also formed when preparing **7**.

Complexes **9** and **10** were characterized by NMR and MS. In the ^1H NMR spectrum of **9** and **10** the resonances of the CH_2CH_2 unit were found at δ 3.74 and δ 2.37 for **9** and δ 3.70 and δ 2.32 for **10**. Furthermore, the diagnostic resonances of the *i*-Pr and *t*-Bu methyl groups were found at δ 1.16 and δ 1.21 respectively. A NOE correlation between the CH_2CH_2 protons and $H^{6'}$ (for numbering, see Scheme 2) was observed for both complexes, indicating that the reactions had occurred *trans* to tpy-*N*. In the ^{19}F NMR spectra of **9** and **10** one resonace was observed at δ −77.0 corresponding to the OAc^F ligand *trans* to tpy-*C*.

Interestingly, in all complexes **6**−**10** the OAc^F ligand remains in place *trans* to tpy-*C* even in the presence of large excess of other possible ligands which could have coordinated instead. This strong preference for OAc^F *trans* to tpy-*C* was further demonstrated in an experiment where **1** was refluxed in HOAc for 7 days (see SI for details), leading to a nearly selective exchange of the OAc^F group *trans* to tpy-*N* with OAc while the OAc^F group *trans* to tpy-*C* remained in place. Thus, while the site *trans* to tpy-*C* is kinetically more accessible,[21] the thermodynamic preference of a low *trans* influence ligand (i.e., OAc^F over OAc and other possible ligands) controls the observed product selectivity. The same selectivity was observed

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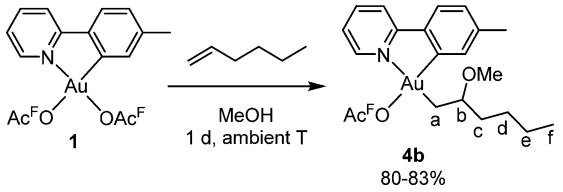
in MeOH, as stirring **1** in MeOH led to a slow exchange of the OAc^F ligand *trans* to tpy-*N* with OMe (see SI for details).

1-Hexene with Methanol as Nucleophile. With the success of MeOH as a nucleophile, and since **4a** was not stable enough to be isolated, the reaction of 1-hexene with **1** was repeated in methanol. After 1 d, the stable product **4b** could be isolated in good yield (Scheme 6). Complex **4b** was

Scheme 6. Nucleophilic Addition of MeOH to 1-Hexene at 1 Furnishing 4b[a]



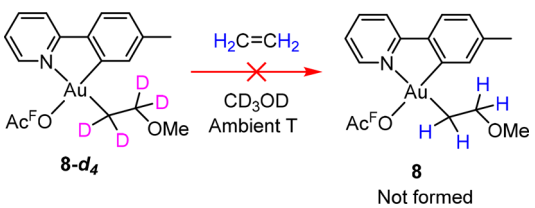
[a]The atoms in the former 1-hexene unit are labeled a–f to simplify the NMR discussions.

characterized by NMR, MS, X-ray diffraction analysis (vide infra), and elemental analysis. The ^{1}H NMR spectrum of **4b** resembles **4a**, but there are some characteristic differences. The signal due to H^b is at δ 3.52 in **4b**, whereas in **4a** it appears at δ 5.40 due to the more electron withdrawing OAc^F bound to the same C as H^b in **4a**. In **4b** the resonance of the OMe group is found at δ 3.39 (similar to the methoxy group in **8** at δ 3.38) and the two diastereotopic H^a are found at δ 2.44–2.47 (overlaps with tpy-CH_3) and δ 2.36 ($^2J_{HH}$ = 9.9 Hz). Only one resonance is observed in the ^{19}F NMR at δ −77.1 corresponding to the OAc^F group *trans* to tpy-C. A NOE correlation between H^a and $H^{6'}$, and between H^b and $H^{6'}$ (for numbering, see Scheme 2) indicates that the reaction has occurred in the position *trans* to tpy-*N*.

We were intrigued by the remarkable stability difference of **4a** and **4b** and sought to gain more insight into this phenomenon. As was previously reported by us, the nucleophilic addition of $^-OAc^F$ to ethylene at **1** (Scheme 1, top) was found to be reversible.[21] Since $^-$OMe is a poorer leaving group than $^-OAc^F$ it was hypothesized that this could slow down the reverse reaction and thus increase the stability of the methoxy products. It was indeed found that upon treating **8-d_4** with unlabeled ethylene, no formation of unlabeled **8** was observed by ^{1}H NMR monitoring over 4 days indicating that the nucleophilic addition is not reversible under these reaction conditions (Scheme 7).

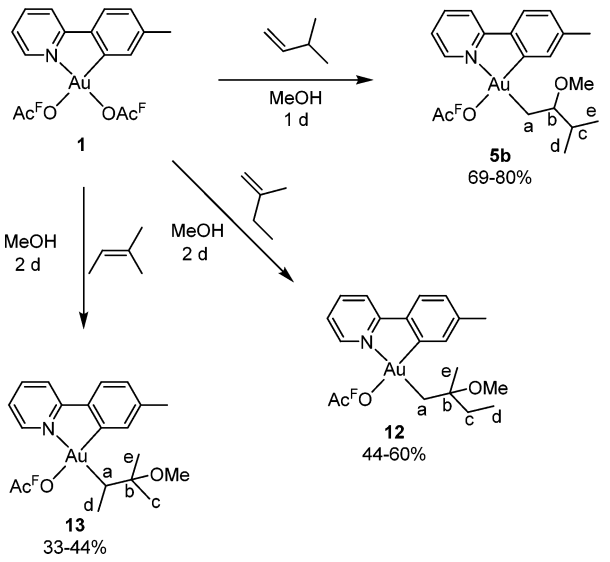
Substituted Butenes with Methanol as Nucleophile. Four butenes with different degrees of substitution were investigated. It was possible to perform a nucleophilic addition of MeOH to the monosubstituted alkene 3-methyl-1-butene, the disubstituted alkene 2-methyl-1-butene, and even the

Scheme 7. Treating 8-d_4 with Unlabeled Ethylene Did Not Lead to Any Formation of 8



trisubstituted alkene 2-methyl-2-butene furnishing **5b**, **12**, and **13** respectively (Scheme 8). However, the yields drop with

Scheme 8. Nucleophilic Addition of MeOH to a Series of Mono-, Di-, and Trisubstituted Butenes at 1 Furnishing 5b, 12, and 13[a]



[a]All the reactions depicted in this scheme were performed at ambient temperature. The atoms in the former alkene units are labeled a–e to simplify the NMR discussions.

increasing alkene substitution. In **5b**, **12**, and **13** the nucleophilic addition occurs at the most substituted site of the double bond in agreement with previous observations. The tetrasubstituted alkene 2,3-dimethyl-2-butene (not shown in Scheme 8), did not react with **1** under these conditions (see SI for details).

Complex **5b** was characterized by NMR, MS, X-ray diffraction analysis (vide infra), and elemental analysis. The ^{1}H NMR of **5b** is rather similar to that of **5a**, the most prominent change being the shift of the resonance of H^b from δ 5.31 in **5a** to δ 3.35 in **5b** which is rather similar to what was observed for H^b in **4b** (δ 3.52) and $\underline{CH_2}$OMe in **8** (δ 3.68). The resonance of the OMe group is found at δ 3.40 consistent with what was observed in **4a** and **8**. The two diastereotopic H^a are at δ 2.43–2.46 (overlaps with tpy-CH_3) and δ 2.30 ($^2J_{HH}$ = 10.0 Hz) and the two diastereotopic methyl groups are found as two partly overlapping doublets at δ 0.98–1.00. A NOE correlation could be observed between H^a and $H^{6'}$ and H^b and $H^{6'}$ (see Scheme 2 for numbering) indicating that the reaction has occurred in the position *trans* to tpy-*N*.

For the syntheses of **12** and **13**, a prolonged reaction time compared to **5b** was needed. Complexes **12** and **13** were prepared in moderate to low yields and were characterized by NMR, MS, and elemental analysis. **13** was also characterized by X-ray diffraction analysis (vide infra). In the ^{1}H NMR spectrum of **12** the OMe resonance is found at δ 3.19, at slightly smaller ppm than that observed for **4b**, **5b**, and **8**. The two diastereotopic H^a are found at δ 2.59 and δ 2.53 ($^2J_{HH}$ = 10.3 Hz), CH_3^e is a singlet at δ 1.33, CH_3^d is an apparent triplet at δ 0.95, and the two diastereotopic H^c are at δ 1.75 and δ 1.70. A NOE correlation could be observed between H^a and $H^{6'}$ and CH_3^e and $H^{6'}$ (for numbering, see Scheme 2) indicating that the reaction has occurred in the position *trans* to tpy-*N*. In the

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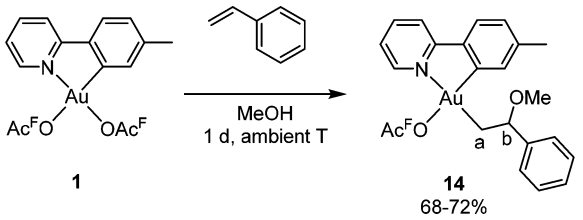
^{1}H NMR spectrum of **13** H^a is found as a quartet at δ 2.91, at slightly larger ppm than what was observed for H^a in **5b** and **12**. The three methyl groups CH_3^c, CH_3^d, and CH_3^e are found as overlapping signals at δ 1.28−1.36 and the OMe resonance is found at δ 3.21 similar to what was observed for **12**. For all three complexes **5b**, **12**, and **13** one signal corresponding to the OAc^F ligand *trans* to tpy-*C* is observed in the ^{19}F NMR spectra at δ −77.0, −77.1, and −77.3 respectively.

Styrene with Methanol as Nucleophile. We were interested to see if the conjugated double bond in styrene would react in the same way as the alkenes described herein. It turned out that it was possible to perform a nucleophilic addition of MeOH to styrene furnishing **14** (Scheme 9). The reaction occurred *trans* to tpy-*N* and the nucleophilic addition occurred at the internal position of the double bond in agreement with previous findings.

Scheme 9. Nucleophilic Addition of MeOH to Styrene at 1 Furnishing 14[a]



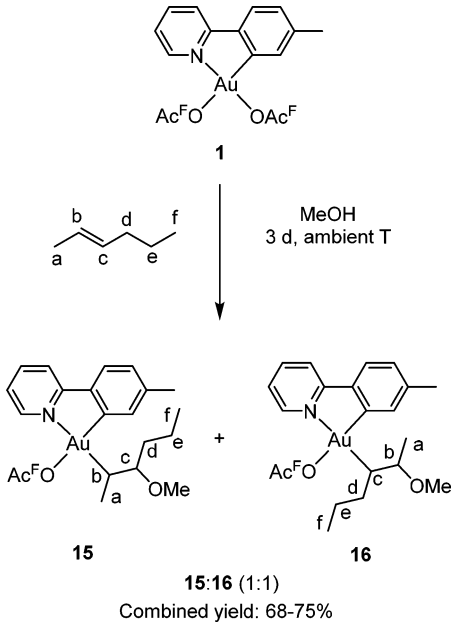
1 **14** 68-72%

[a]The atoms in the former double bond are labeled a−b to simplify the NMR discussions.

Complex **14** was characterized by NMR, MS, X-ray diffraction analysis (as the CH_2Cl_2 solvate, vide infra), and elemental analysis. In the ^{1}H NMR spectrum of **14** the characteristic resonances of the phenyl substituent are observed at δ 7.44, δ 7.36, and δ 7.28. The OMe resonance is found at δ 3.23, similar to what was observed for **12** and **13**, and at slightly smaller ppm values than those for **8**, **5b**, and **4b**. A doublet of doublets at δ 4.55 corresponds to H^b which is at larger ppm values than those observed for **4b** (δ 3.52), **5b** (δ 3.35), and **8** (OCH_2 δ 3.68), probably due to the electron withdrawing phenyl group. The two diastereotopic H^a are found at δ 2.63 and δ 2.50 ($^2J_{HH}$ = 10.3 and 10.2 Hz). One signal at δ −77.0 was observed in the ^{19}F NMR spectrum corresponding to the OAc^F ligand *trans* to tpy-*C*.

***trans*-2-Hexene with Methanol as Nucleophile.** Throughout this study, we have observed a selectivity for the nucleophilic addition to occur at the most substituted site of the double bond. We were therefore interested in the preferred selectivity with the 2,3-disubstituted alkene *trans*-2-hexene. When performing the reaction a mixture of the two isomers **15** and **16** (Scheme 10) was obtained in an approximately 1:1 ratio as could be observed by ^{1}H NMR of the reaction mixture (see SI). Several of the resonances in the ^{1}H NMR spectrum of the two isomers are at similar chemical shifts and are therefore overlapping, but for some signals there is a significant difference. In the tpy ligand, the difference between the two isomers is clearly seen for H^6 and H$^{6'}$ (see Scheme 2 for numbering). The difference between the two isomers is also clearly discernible for the OMe resonance, the triplets and doublets belonging to the two CH_3 units in the C_6-alkyl chain and H^b. H^b is found at δ 2.62 in **15** and δ 3.55 in **16**, the larger ppm value of H^b in **16** compared to **15** indicates that the

Scheme 10. Nucleophilic Addition of MeOH to *trans*-2-Hexene Furnishing a Mixture of the Two Isomers 15 and 16 in an Approximately 1:1 Ratio[a]



1 **15** **16**

15:**16** (1:1)
Combined yield: 68-75%

[a]The two isomers originate from nucleophilic addition at both sites of the double bond. The atoms in the former *trans*-2-hexene unit are labeled a−f to simplify the NMR discussions.

nucleophilic addition has occurred at C^b in **16** and at at C^c in **15**. No interconversion of the two isomers could be observed by ^{1}H NMR in CD_2Cl_2 over time, in agreement with the nonreversibility of the ethylene reaction in MeOH described previously. Crystallization of the isomer mixture led to formation of two types of crystals with different morphology; large crystals belonging to **15** and small crystals belonging to **16** (see SI). These two isomers could be separated by picking crystals under a microscope and single crystal X-ray diffraction analyses (vide infra) and NMR characterization were performed using the crystals of both isomers.

We previously reported that the nucleophilic addition of $^-OAc^F$ to ethylene[21] and acetylene[22] at **1** occurred in an *anti* fashion. In **15** and **16** it is also possible to distinguish whether the nucleophilic addition occurs in an *anti* or *syn* fashion from the solid state structures of **15** and **16**. One pair of diastereomers will be formed from *anti* addition (R,S and S,R) and another pair would be formed from *syn* addition (S,S and R,R). In the solid state structures of **15** and **16** (vide infra) it is clear that the nucleophilic addition of MeOH to *trans*-2-hexene occurred in an *anti* fashion, in agreement with previous findings.

Crystallographic Structure Determination. Complexes **4b**, **5a** (as the $CHCl_3$ solvate), **5b**, **6**, **8**, **13**, **14** (as the CH_2Cl_2 solvate), **15**, and **16** have been characterized by X-ray diffraction analysis and their ORTEPs are given in Figure 1 and Figure 2 together with selected metrical parameters in Table 1 and Table 2. In **6** and **14** the asymmetric unit consists of two complexes, and the metrical parameters are given for both complexes. As expected, all the structurally characterized complexes reported herein have the nearly square planar geometry that is commonly observed for Au(III) complexes. The structures are in full agreement with the NMR data and verify that the reactions have occurred *trans* to tpy-*N* while the

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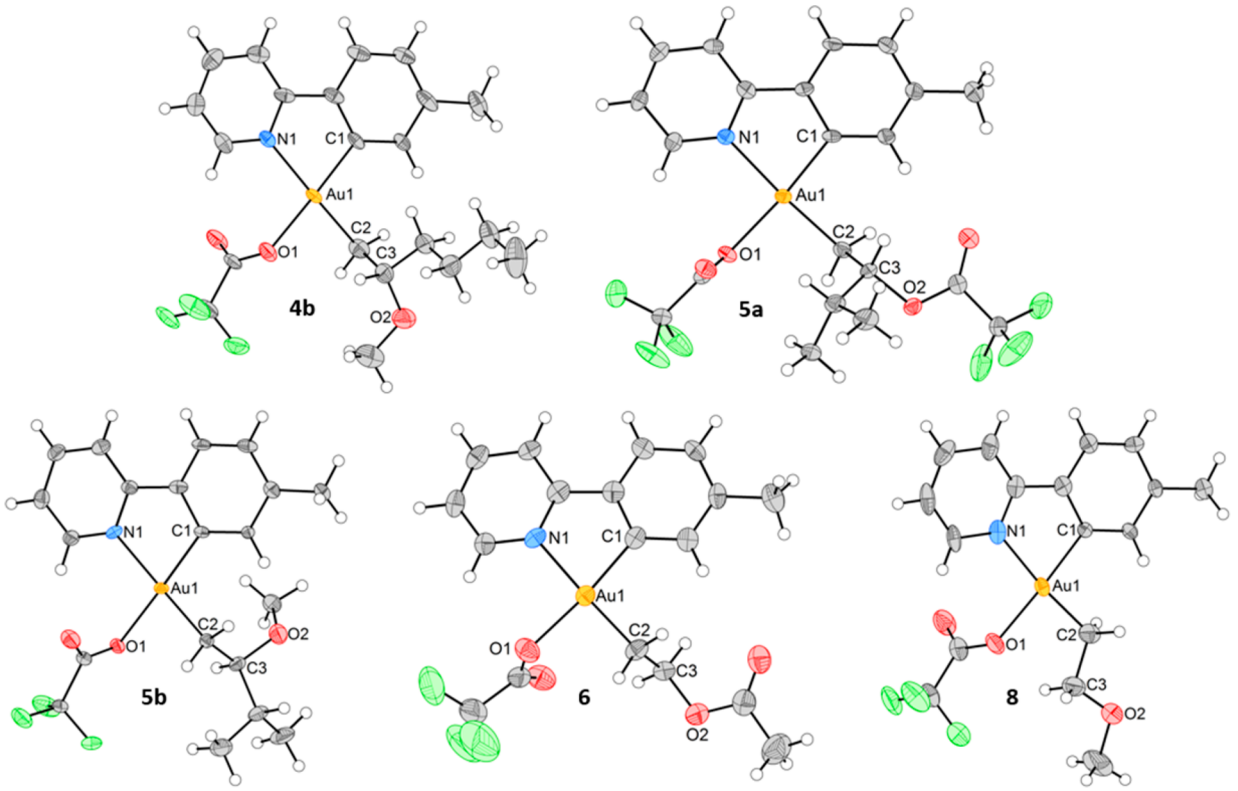

Figure 1. ORTEP plot of **4b**, **5a**,**b**, **6**, and **8** with 50% ellipsoids. For **5a**, the $CHCl_3$ solvent of crystallization was removed for clarity.

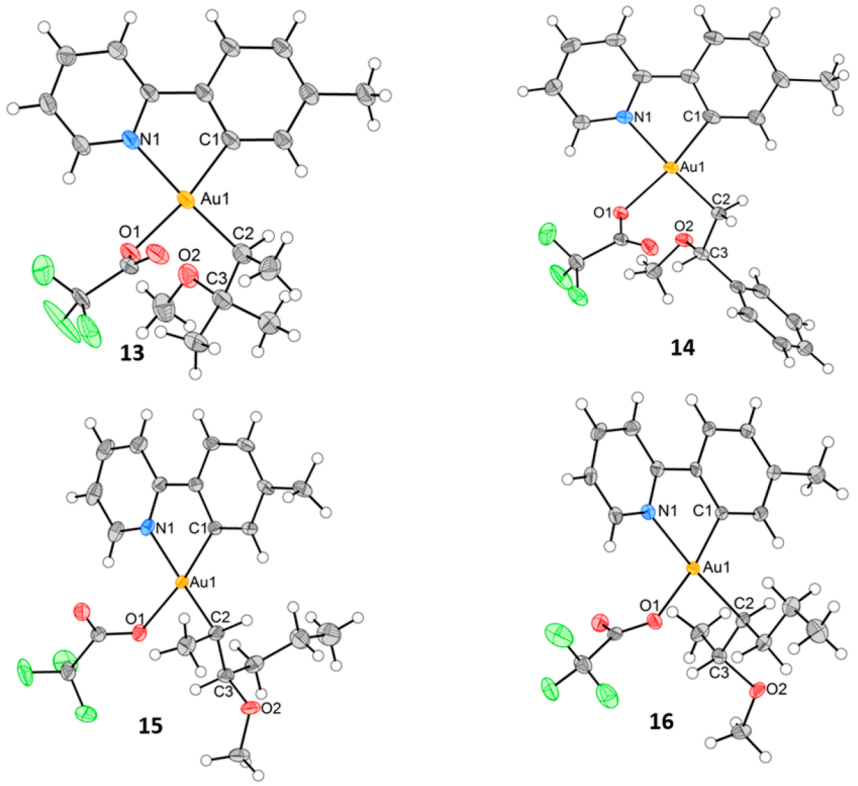

Figure 2. ORTEP plot of **13**−**16** with 50% ellipsoids. For **14**, the CH_2CH_2 solvent of crystallization was removed for clarity. In **13** and **14** the OAc^F ligand is disordered (see SI).

OAc^F ligand remains in place *trans* to tpy-C. In the solid state structures of **4a**, **5a**,**b**, **13** and **14** it is evident that the nucleophilic additions have occurred at most substituted site of the double bond. A slight deviation of the N1−Au1−C1 chelate angle from the idealized 90° is observed in all the complexes, ranging from 81.1(3) in **6** to 81.95(10)° in **14**, in agreement

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Table 1. Selected Bond Distances [Å] and Angles [°] for 4b, 5a,b, 6, and 8[a]

	4b	5a	5b	6	8
Au1−N1	2.117(7)	2.110(5)	2.108(8)	2.104(6), 2.094(6)	2.089(11)
Au1−C1	1.999(8)	2.013(5)	1.998(9)	2.002(7), 2.014(7)	2.018(10)
Au1−O1	2.109(6)	2.114(3)	2.115(7)	2.087(6), 2.101(5)	2.102(9)
Au1−C2	2.025(9)	2.045(5)	2.055(9)	2.043(7), 2.023(8)	2.012(15)
C2−C3	1.517(13)	1.512(7)	1.526(13)	1.521(11), 1.522(10)	1.522(17)
C3−O2	1.426(13)	1.503(6)	1.433(13)	1.463(9), 1.447(9)	1.41(2)
O1−Au1−N1	96.0(3)	93.88(15)	96.4(3)	93.3(2), 92.1(2)	95.1(4)
N1−Au1−C1	81.6(3)	81.57(19)	81.5(4)	81.3(3), 81.1(3)	81.5(4)
C1−Au1−C2	96.6(4)	94.9(2)	96.2(4)	96.1(3), 95.7(3)	92.0(5)
C2−Au1−O1	85.8(3)	89.55(18)	86.0(3)	89.4(3), 91.0(3)	91.5(5)
C1−Au1−O1	177.1(3)	174.82(18)	177.5(4)	174.2(3), 173.1(3)	176.4(5)
N1−Au1−C2	177.9(3)	176.02(18)	175.3(3)	177.2(3), 176.3(3)	173.3(5)

[a]In 6 the asymmetric unit consists of two complexes and the metrical parameters for both complexes are given.

Table 2. Selected Bond Distances [Å] and Angles [°] for 13−16[a]

	13	14	15	16
Au1−N1	2.137(3)	2.113(2), 2.126(2)	2.131(2)	2.127(3)
Au1−C1	2.012(3)	2.002(2), 2.010(2)	2.007(3)	2.009(4)
Au1−O1	2.111(2)	2.1022(18), 2.1159(17)	2.110(2)	2.116(3)
Au1−C2	2.080(4)	2.044(3), 2.054(2)	2.069(3)	2.074(4)
C2−C3	1.549(5)	1.513(3), 1.523(3)	1.520(4)	1.522(6)
C3−O2	1.439(5)	1.424(3), 1.425(3)	1.441(4)	1.448(5)
O1−Au1−N1	89.62(10)	88.90(8), 91.20(8)	91.92(9)	91.94(12
N1−Au1−C1	81.38(12)	81.95(10), 81.44(10)	81.72(10)	81.44(14)
C1−Au1−C2	93.79(14)	94.07(11), 92.80(10)	95.89(11)	96.81(16)
C2−Au1−O1	95.31(12)	95.09(9), 94.63(9)	90.39(19)	90.14(14)
C1−Au1−O1	170.81(12)	170.84(10), 172.50(9)	172.19(9)	172.51(13)
N1−Au1−C2	173.84(12)	175.07(10), 173.14(9)	177.44(10)	173.79(15)

[a]In 14 the asymmetric unit consists of two complexes and the metrical parameters for both complexes are given.

with that observed in the related complexes **1**,[23] **2**,[21] **3**,[21] Au(OAc^F)(CHCHOAc^F)(tpy),[22] Au(OAc^F)(CH$_2$CHO)(tpy),[22] and the metallacycle [Au(NH=C(CH$_3$)OCH$_2$CH$_2$)(tpy)]$^+$[OAc^F]$^-$[24] reported previously. The Au1−N1 ligand distances, the Au1−O1 distances, and the Au1−C1 distances are in the range of, or slightly longer, than that reported for related complexes.[21−24] The shortest Au−C2 ligand distances are those of **8**, 2.012(15) Å, followed by **6** and **4b** with 2.023(8) and 2.025(9) Å respectively. On the longer side is **13** with 2.080 (4) Å followed by **15** and **16** with 2.075(4) and 2.069(3) Å respectively. The Au−C2 distances in **5a**,**b**, **6**, and **14** range from 2.043(7) to 2.055(9) Å and are similar to, or slightly longer, than those of **2**[21] and **3**[21] at 2.042(3) and 2.040(4) Å, respectively.

Relevance for Catalysis. The design of a catalytic process based on the reactions described herein would lead to very useful methods to prepare esters and ethers from simple and readily available building blocks under mild reaction conditions. However, the reactions discussed herein come to a stop after the first alkene functionalization *trans* to tpy-*N* and no catalytic processes could be achieved. Experiments where HOAc^F was added to a mixture of the insertion product, excess alkene and solvent/nucleophile (see SI for details) did not lead to any catalysis and the complexes remained stable in solution over several days. For example, treatment of **8-d_3** (generated in situ from **1** and ethylene in CD$_3$OD) with HOAc^F in the presence of excess ethylene did not furnish the ether product expected from protodeauration, even after heating at elevated temperatures (50−60 °C). Also, adding HOAc^F to a mixture of the more sterically crowded **13** and 2-methyl-2-butene in CD$_3$OD did not lead to the expected protodeauration product; however, in this case decomposition occurred to unknown products. Based on our recent report of a catalytic functionalization of acetylene with **1** as a precatalyst furnishing vinyl trifluoroacetate[22] it seems that two main challenges must be overcome in order to achieve catalysis with the system described herein: (i) the *trans* to tpy-*N* vs *trans* to tpy-*C* situation must be controlled: in Au(CHCHOAc^F)$_2$(tpy) only the vinyl group *trans* to tpy-*C* undergoes protolytic cleavage in HOAc^F while the vinyl group *trans* to tpy-*N* remains intact.[22] (ii) The preference for protolytic cleavage of Au−C(sp^2) bonds over Au−C(sp^3) bonds must be circumvented (in Au(tpy)Me$_2$ the preference for protolytic cleavage at Au−C(sp^2) over Au−C(sp^3) was demonstrated[25]), for example by replacing the C(sp^2)-end of the tpy chelate with a Au−C(sp^3) bound ligand.

CONCLUSIONS

This work has provided a detailed study of functionalization of alkenes at Au(III) furnishing several new Au(III) complexes bearing C(sp^3) bonded ligands. Insight into the scope and regiochemistry of the nucleophilic addition to alkenes at Au(III) has been obtained. The reactions of a range of different alkenes with various substitution patterns have been investigated with several different oxygen-based nucleophiles. In all the cases studied, the reactions occur *trans* to tpy-*N* reflecting the strong thermodynamic preference of the high *trans* influence C(sp^3) group to bind *trans* to the weaker *trans* influence tpy-*N*, and not *trans* to the high *trans* influence tpy-C(sp^2). *Trans* to tpy-*C*, the lower *trans* influence OAc^F ligand always remains in place. Furthermore, the nucleophilic additions exclusively occurred at the most substituted site of the double bond, in a Markovnikov manner. For the 2,3-disubstituted alkene *trans*-2-hexene, where both sites of the alkene bears one substituent, a mixture of the two isomers

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resulting from nucleophilic addition at both sites of the alkenes was obtained. With *trans*-2-hexene it was also found that the nucleophilic addition occurred in an *anti* fashion, in agreement with previous findings.[21,22] The insight gained through this study is of great importance for further developing and understanding Au(III) catalysis and alkene functionalization.

EXPERIMENTAL SECTION

Au(III) complexes **1** and **2** were prepared by previously reported procedures.[21,23] CH_2Cl_2 was purified using a MB SPS-800 solvent purifying system from MBraun. CD_2Cl_2, MeOH, EtOH, *i*-PrOH, and *t*-BuOH were dried over 3 Å molecular sieves. HOAc, $HOAc^F$, DOAc, $DOAc^F$, CD_3OD, CD_3CD_2OD, and pentane were used as received. Ethylene 3.5 was purchased from Hydro Gas. All complexes were synthesized in air and inert atmosphere was only utilized for the storage of the complexes and the work up of **7**, **9**, and **10**. For the synthesis of **7**, **9**, and **10** dry conditions were needed in order to minimize byproduct formation. In these cases all equipment and chemicals were dried prior to use and ethylene was dried by passing it through a 3 Å molecular sieve trap. As a precaution, all syntheses were performed in the absence of light. NMR spectra were recorded on Bruker Avance DPX200, DPX300, AVII400, DRX500, AV600, AVII600, and AVIIIHD800 instruments at ambient temperature. ^1H and ^{13}C NMR spectra have been referenced relative to the residual solvent signals (CD_2Cl_2 $\delta(^1H)$ 5.34, $\delta(^{13}C)$ 53.84; $HOAc^F$ $\delta(^1H)$ 11.50; CD_3OD $\delta(^1H)$ 3.31, δ (^{13}C) 49.00; CD_3CD_2OD $\delta(^1H)$ 1.11, 3.55; HOAc $\delta(^1H)$ 2.03). ^{19}F has been referenced to $CFCl_3$ by using C_6F_6 (−164.9 ppm with respect to $CFCl_3$ at 0 ppm) as an internal standard by adding ca. 0.5−1 μL C_6F_6 to the NMR sample. The peaks in the ^1H NMR and ^{19}F NMR spectra were assigned by the aid of 2D NMR techniques such as HSQC, HMBC, COSY, NOESY, and $^{19}F-^1H$ HOESY according to the numbering scheme shown in Figure 3. Mass spectra (ESI) were obtained on a Micromass QTOF II

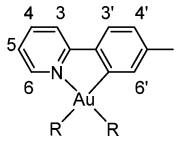

Figure 3. Numbering scheme used for reporting the NMR data.

spectrometer and a Bruker maXis II ETD spectrometer by Osamu Sekiguchi, University of Oslo. Elemental analysis was performed by Microanalytisches Laboratorium Kolbe, Mülheim an der Ruhr, Germany. For each compound the typical yield range is given. In some cases, yields outside of these ranges were obtained. The purity of isolated complexes **4b**, **5a**,**b**, **6**, **8**, **12**, **13**, and **14** were assessed by elemental analysis, high field ^1H NMR (600 or 800 MHz), and ^{19}F NMR (188 MHz). For the remaining complexes, purity was only assessed by high field ^1H NMR (500, 600, or 800 MHz) together with ^{19}F NMR (188 MHz). For the complexes not characterized by elemental analysis (due to sample instability or formation of product mixtures), the presence of NMR silent impurities cannot be excluded. Homogenous NMR samples were always used when assessing the purity by NMR.

The synthesis and characterization of some selected complexes are given here below. For all experimental procedures, see SI.

Generation of Complex 4a in $DOAc^F$. **1** (6.0 mg, 0.010 mmol, 1.0 equiv) was dissolved in CF_3COOD and transferred to a NMR tube. 1,2-dichloroethane (0.5 μL) was added as an internal standard (ISTD). 1-Hexene (1.0 μL, 0.0081 mmol, 0.8 equiv) was added and the reaction was monitored by ^1H NMR (500 MHz). After <10 min, all of $Au(OAc^F)_2(tpy)$ is consumed and **4a** has been formed. **4a** is unstable in $DOAc^F$, and after 3 h ca. 40% of **4a** had decomposed. After 20 h only traces of **4a** were observed in the solution, and the solution contained $tpyD_2^+$ (confirmed by spiking the sample with commercial tpyH), and several other unidentified decomposition products. Due to its instability, **4a** was not isolated. Generation of **4a** in CD_2Cl_2 with $HOAc^F$ added. 1 (14.0 mg, 0.0237 mmol, 1.0 equiv) was dissolved in CD_2Cl_2. $HOAc^F$ (10 μL, 0.13 mmol, 5.5 equiv) and 1-hexene (2.0 μL, 0.016 mmol, 0.7 equiv) were added. The reaction was monitored by ^1H NMR (600 or 500 MHz) and when it was complete, characterization by NMR was performed. For the ^{19}F NMR, a sample without excess $HOAc^F$ was prepared. ^1H NMR (500 MHz, CD_2Cl_2) δ 8.36 (br. d, 1H, J = 4.6 Hz, H^6), 8.08 (ddd, 1H, J 1.6, 7.9, 7.9 Hz, H^4), 7.97 (d, 1H, J = 8.2 Hz, H^3), 7.67 (d, 1H, J = 7.9 Hz, $H^{3'}$), 7.52 (ddd, 1H, J = 1.2, 5.6, 7.5 Hz, H^5), 7.46 (s, 1H, $H^{6'}$), 7.27 (d, 1H, J = 8.0 Hz, $H^{4'}$), 5.40 (m, 1H, H^b), 2.46−2.50 (m, 4H, $ArCH_3$ and H^a), 2.42 (dd, 1H, J = 10.4, 6.9 Hz, H^a), 1.88−2.01 (m, 2H, H^c), 1.20−1.50 (m, 4H, H^d and H^e), 0.91 (t, 3H, J = 7.1 Hz, CH_3^f). ^1H NMR (500 MHz, $HOAc^F$) δ 8.38 (d, 1H, J = 5.1 Hz, H^6), 8.02 (m, 1H, H^4), 7.93 (d, 1H, J = 8.1 Hz, H^3), 7.60 (d, 1H, J = 7.9 Hz, $H^{3'}$), 7.46 (m, 1H, H^5), 7.27 (s, 1H, $H^{6'}$), 7.20 (d, 1H, J = 7.9, $H^{4'}$), 5.42 (m, 1H, H^b), 2.59 (dd, 1H, J = 11.4, 4.8 Hz, H^a). 2.46 (dd, 1H, J = 11.1, 8.9 Hz, H^a), 2.38 (s, 3H, $ArCH_3$), 1.92−2.03 (m, 2H, H^c), 1.31−1.53 (m, 4H, H^d + H^e), 0.88 (t, 3H, J = 7.2 Hz, CH_3^f). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 160.7, 146.5, 143.4, 142.3, 140.5, 135.7, 132.5, 129.8, 126.1, 124.6, 120.5, 81.4, 36.4, 33.7, 28.0, 22.7, 21.9, 13.9. Due to the excess $HOAc^F$ in the sample the carbons arising from the two OAc^F groups could not be assigned (see SI). ^{19}F NMR (188 MHz, CD_2Cl_2) δ −77.1 (OAc^F trans to tpy-*C*), −78.0 (OAc^F trans to tpy-*N*).

Preparation of Complex 4b. MeOH (5 mL) was added to **1** (50.0 mg, 0.0846 mmol, 1.0 equiv). 1-Hexene (21 μL, 0.17 mmol, 2.0 equiv) was added. The flask was sealed with a glass stopper and the reaction mixture was stirred at ambient temperature in the absence of light for 1 d. The volatiles were removed under reduced pressure and the remaining solid was dissolved in CH_2Cl_2 and filtered. CH_2Cl_2 was removed under reduced pressure furnishing **4b** (40.0 mg, 0.0674 mmol, 80%) as a white solid. ^1H NMR (600 MHz, CD_2Cl_2) δ 8.43 (d, 1H, J = 4.68 Hz, H^6), 8.04 (ddd, 1H, J = 8.0, 8.0, 1.56 Hz, H^4), 7.96 (d, 1H, J = 8.16 Hz, H^3), 7.68 (d, 1H, J = 7.92 Hz, $H^{3'}$), 7.49 (ddd, 1H, J = 7.32, 5.58, 1.02, H^5), 7.44 (s, 1H, H6′), 7.23 (d, 1H, J = 7.8 Hz, $H^{4'}$), 3.52 (m, 1H, H^b), 3.39 (s, 3H, OCH_3), 2.44−2.47 (m, 4H, H^a and $ArCH_3$), 2.36 (dd, 1H, J = 9.9, 6.7 Hz, H^a), 1.69 (m, 2H, H^c), 1.50−1.29 (m, 4H, H^d and H^e), 0.91 (t, 3H, J = 7.2 Hz, CH_3^f). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 161.2 (q, J = 36.8, O<u>C</u>OCF$_3$), 160.7, 146.6, 142.5, 141.7, 141.1, 136.8, 132.8, 129.1, 125.7, 124.3, 120.2, 118.3 (q, J = 290.1, OCO<u>C</u>F3), 81.3, 56.8, 38.3, 36.7, 28.4, 23.2, 22.0, 14.3. ^{19}F NMR (188 MHz, CD2Cl2) δ −77.1 (OAC^F). MS (ESI, MeOH) m/z (rel. %) 1053 (41), 538 (100), 480 ([M − OAc^F]$^+$, 49]. HRMS (ESI, MeOH) found: 480.1593; calcd for $C_{19}H_{25}AuNO$: 480.1596. Elemental analysis Anal. Calcd for $C_{21}H_{25}AuNO_3F_3$: C, 42.51; H, 4.25; N, 2.36. Found: C, 42.52; H, 4.21; N, 2.30. The sample for the elemental analysis was taken from the bulk material prepared as described above. The batch used for the elemental analysis was obtained in 58% yield.

Preparation of Complex 5a. **1** (50.0 mg, 0.0846 mmol) was dissolved in CH_2Cl_2 (5 mL). 3-Methyl-1-butene (ca. 20 μL) was added and the flask was sealed with a glass stopper. The reaction mixture was stirred at ambient temperature in the absence of light for 1 d. The volatiles were removed under reduced pressure and the remaining solid was dissolved in CH_2Cl_2 and filtered. The solvent was removed under reduced pressure furnishing **5a** (43.2 mg, 0.0653 mmol, 77%) as a white solid. Due to the volatility of 3-methyl-1-butene it could not be measured out with a microliter syringe and it was added with a glass pipet (ca. 1 drop) instead. The reaction with 3-methyl-1-butene has to be performed in CH_2Cl_2 and not in $HOAc^F$ due to the instability of the alkene in the acidic media. ^1H NMR (600 MHz, CD_2Cl_2) δ 8.40 (dd, 1H, J = 0.7, 5.5 Hz, H^6), 8.06 (ddd, 1H, J = 1.6, 7.9, 7.9 Hz, H^4), 7.96 (d, 1H, J = 8.1 Hz, H^3), 7.66 (d, 1H, J = 7.9 Hz, $H^{3'}$), 7.50 (ddd, 1H, J = 1.1, 5.6, 7.4 Hz, H^5), 7.47 (s, 1H, $H^{6'}$), 7.25 (dd, 1H, J = 0.3, 7.9 Hz, $H^{4'}$), 5.31 (ddd, 1H, J = 4.2, 6.3, 7.7 Hz, H^b), 2.60 (dd, 1H, J = 6.3, 10.7 Hz, H^a), 2.47 (s, 3H, $ArCH_3$), 2.32 (dd, 1H, J = 7.8, 10.7 Hz, H^a), 2.21 (m, 1H, H^c), 1.07 (d, 3H, J = 6.8 Hz, CH_3^d or CH_3^e), 1.05 (d, 3H, J = 6.8 Hz, CH_3^d or CH_3^e). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 161.3 ppm (q, J = 37.3 Hz, O<u>C</u>OCF$_3$), 161.0, 157.6 (q, J = 41.6 Hz, O<u>C</u>OCF$_3$), 146.5, 143.1, 142.1, 140.8, 136.5,

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132.6, 129.4, 125.9, 124.4, 120.4, 118.2 (q, J = 290.1 Hz, OCO$\underline{C}F_3$), 115.0 (q, J = 286.4 Hz, OCO$\underline{C}F_3$), 85.2, 33.7, 30.5, 21.9, 19.2, 16.7. ^{19}F NMR (188 MHz, CD_2Cl_2) δ −77.0 (OAc^F *trans* to tpy-*C*), −77.9 (OAc^F *trans* to tpy-*N*). MS (ESI, MeCN) m/z (rel. %) 548 ([M − OAc^F]$^+$, 6), 493 (100), 474 (13), 434 (54), 423 (13). HRMS (ESI, MeCN) found: 548.1103; calcd for $C_{19}H_{20}AuF_3NO_2$: 548.1106. Elemental analysis: Anal. Calcd for $C_{21}H_{20}AuNO_4F_6$: C, 38.14; H, 3.05; N, 2.12. Found: C, 38.54; H, 3.30; N, 2.20. The sample for the elemental analysis was taken from the bulk material prepared as described above. The batch used for the elemental analysis was obtained in 55% yield.

Preparation of Complex 5b. MeOH (5 mL) was added to **1** (50.0 mg, 0.0846 mmol). 3-Methyl-1-butene (ca. 20 μL) was added and the flask was sealed with a glass stopper. The reaction mixture was stirred at ambient temperature in the absence of light for 1 d. The volatiles were removed under reduced pressure and the remaining solid was dissolved in CH_2Cl_2 and filtered. The solvent was removed under reduced pressure furnishing **5b** (39.4 mg, 0.0680 mmol, 80%) as a white solid. Due to the volatility of 3-methyl-1-butene it could not be measured out with a microliter syringe and it was added with a glass pipet (ca. 1 drop) instead. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.42 (d, 1H, J = 5.3 Hz, H^6), 8.03 (ddd, 1H, J = 7.9, 7.9, 1.6 Hz, H^4), 7.96 (d, 1H, J = 8.1 Hz, H^3), 7.68 (d, 1H, J = 7.9 Hz, $H^{3'}$), 7.48 (ddd, 1H, J = 1.0, 5.6, 7.4 Hz, H^5), 7.45 (s, 1H, $H^{6'}$), 7.22 (d, 1H, J = 7.8 Hz, $H^{4'}$), 3.40 (s, 3H, OCH_3), 3.35 (ddd, 1H, J = 4.4, 5.6, 7.7 Hz, H^b), 2.43−2.46 (m, 4H, $ArCH_3$ and H^a), 2.30 (dd, 1H, J = 7.9, 10.0 Hz, H^a), 2.01 (m, 1H, H^c), 0.98−1.00 (m, 6H, H^d and H^e). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 161.2 (q, J = 36.9 Hz, O$\underline{C}OCF_3$), 160.7, 146.6, 142.5, 141.7, 141.0, 136.9, 132.7, 129.1, 125.7, 124.3, 120.2, 118.3 (q, J = 290.2 Hz, OCO$\underline{C}F_3$), 86.2, 57.8, 35.4, 33.2, 22.0, 18.7, 17.7. ^{19}F NMR (188 MHz, CD_2Cl_2) δ −77.0 (OAc^F). MS (ESI, MeOH) m/z (rel. %) 1025 (34), 524 (100), 466 ([M − OAC^F]$^+$, 50). HRMS (ESI, MeOH) found: 466.1441; calcd for $C_{18}H_{23}AuNO$: 466.1440. Elemental analysis: Anal. Calcd for $C_{20}H_{23}AuNO_3F_3$: C, 41.46; H, 4.00; N, 2.42. Found: C, 41.71; H, 4.18; N, 2.52. The sample for the elemental analysis was taken from the bulk material prepared as described above. The batch used for the elemental analysis was obtained in 80% yield.

Preparation of Complex 6. HOAc (5 mL) was added to **1** (75.4 mg, 0.128 mmol, 1.0 equiv). Ethylene was bubbled through the solution for 2 min, and the flask was sealed with a glass stopper. The reaction mixture was stirred at ambient temperature in the absence of light. After 11 days, ethylene was bubbled through the solution for 1 min and after a total of 12 days the solution was filtered and the volatiles were removed under reduced pressure furnishing **6** (60.8 mg, 0.108 mmol, 84%) as a white fluffy solid. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.40 (d, 1H, J = 5.0 Hz, H^6), 8.05 (ddd, 1H, J = 1.5, 8.0, 8.0 Hz, H^4), 7.95 (d, 1H, J = 8.2 Hz, H^3), 7.66 (d, 1H, J = 7.9 Hz, $H^{3'}$), 7.49 (ddd, 1H, J = 1.0, 5.5, 7.5 Hz, H^5), 7.47 (s, 1H, $H^{6'}$), 7.23 (d, 1H, J = 7.9 Hz, $H^{4'}$), 4.42 (m, 2H, OCH_2), 2.46 (s, 3H, $ArCH_3$), 2.38 (m, 2H, $AuCH_2$), 2.04 (s, 3H, OAc). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 171.3, 161.3 (q, J = 37.0 Hz, O$\underline{C}OCF_3$), 160.9, 146.4, 143.0, 141.9, 140.8, 136.6, 132.4, 129.3, 125.8, 124.4, 120.3, 118.3 (q, J = 290.2 Hz, OCO$\underline{C}F_3$), 64.3, 29.4, 22.0, 21.3. ^{19}F NMR (188 MHz, CD_2Cl_2): −77.0 (OAc^F). MS (ESI, MeCN) m/z (rel. %) 997 (30), 510 (100), 452 ([M − OAc^F]$^+$, 71]). HRMS (ESI, MeCN) found: 452.0919; calcd for $C_{16}H_{17}AuNO_2$: 452.0919. Elemental analysis: Anal. Calcd for $C_{18}H_{17}AuNO_4F_3$: C, 38.24; H, 3.03; N, 2.48. Found: C, 38.36; H, 3.05; N, 2.46. The sample for the elemental analysis was taken from the bulk material prepared as described above. The batch used for the elemental analysis was obtained in 84% yield.

Preparation of Complex 7. EtOH (5 mL) and Na_2SO_4 (ca. 2 g), as a water absorbent, were added to a round-bottom flask and stirred for 5−10 min. **1** (50.3 mg, 0.0851 mmol) was added and the solution was stirred for 15 min. Ethylene was bubbled through the solution for 1 min and the solution was stirred for 3 d at ambient temperature in the absence of light. The volatiles were removed under reduced pressure and the remaining solid was dissolved in CH_2Cl_2 and filtered under Ar. The solvent was removed under reduced pressure furnishing **7** (35 mg, 0.063 mmol, 74%) as a white solid. Small amounts of **11** (<15%) were observed in the ^{1}H NMR spectrum of **7** which presumably originate from the reaction of $Au(OAc^F)_2$(tpy) with ethylene and water. Due to the presence of **11**, the yield of **7** is overestimated. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.41 (ddd, 1H, J = 5.6, 1.3, 0.6 Hz, H^6), 8.04 (ddd, 1H, J = 8.0, 7.7, 1.6 Hz, H^4), 7.95 (d, 1H, J = 8.2 Hz, H^3), 7.67 (d, 1H, J = 7.9 Hz, $H^{3'}$), 7.49 (ddd, 1H, J = 7.5, 5.5, 1.2 Hz, H^5), 7.38 (s, 1H, $H^{6'}$), 7.22 (ddd, 1H, J = 7.9, 1.5, 0.8 Hz, $H^{4'}$), 3.74 (m, 2H, CH_2OEt), 3.55 (q, 2H, J = 7.0 Hz, O$\underline{C}H_2CH_3$), 2.45 (s, 3H $ArCH_3$), 2.40 (m, 2H, $AuCH_2$), 1.19 (t, 3H, J = 7.0 Hz, $OCH_2C\underline{H}_3$). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 161.2 (q, J = 36.8 Hz, O$\underline{C}OCF_3$), 160.7, 146.5, 142.7, 141.8, 141.0, 136.6, 132.3, 129.2, 125.7, 124.3, 120.2, 118.3 (q, J = 290.2 Hz, OCO$\underline{C}F_3$), 69.6, 66.1, 32.4, 22.0, 15.5. ^{19}F NMR (188 MHz, CD_2Cl_2) δ −77.0 (OAC^F). MS (ESI, EtOH) m/z (rel. %) 438 ([M − OAc^F]$^+$, 100). HRMS (ESI, MeCN): Found 438.1138; calcd for $C_{16}H_{19}NOAu$: 438.1132.

Preparation of Complex 8. MeOH (5 mL) was added to **1** (50.0 mg, 0.0846 mmol). Ethylene was bubbled through the solution for 2 min, and the flask was sealed with a glass stopper. The reaction mixture was stirred at ambient temperature in the absence of light for 1 d. The volatiles were removed under reduced pressure and the remaining solid was dissolved in CH_2Cl_2 and filtered. CH_2Cl_2 was removed under reduced pressure furnishing **8** (32.9 mg, 0.0612 mmol, 72%) as a white solid. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.37 (d, 1H, J = 5.5 Hz, H^6), 8.02 (ddd, 1H. J = 1.5, 8.0, 8.0, H^4), 7.94 (d, 1H, J = 8.2, H^3), 7.65 (d, 1H, J = 7.9 Hz, $H^{3'}$), 7.47 (ddd, 1H, J = 0.8 Hz, 5.4, 7.5 Hz, H^5), 7.32 (s, 1H, $H^{6'}$), 7.21 (d, 1H, J = 7.9 Hz, $H^{4'}$), 3.68 (m, 2H, OCH_2), 3.38 (s, 3H, OCH_3), 2.44 (s, 3H, $ArCH_3$), 2.39 (m, 2H, $AuCH_2$). ^{13}C NMR (151 MHz, CD_2Cl_2) δ 161.3 (q, J = 36.8 Hz, O$\underline{C}OCF_3$), 160.7, 146.4, 142.7, 141.8, 140.9, 136.5, 132.1, 129.2, 125.8, 124.3, 120.2, 118.3 (q, J = 290.3 Hz, OCO$\underline{C}F_3$), 72.0, 58.3, 32.1, 22.0. ^{19}F NMR (188 MHz, CD_2Cl_2) δ −77.0 (OAc^F). MS (ESI, MeOH) m/z (rel. %) 941 (36), 482 (100), 424 ([M − OAc^F]$^+$, 33). HRMS (ESI, MeOH) found: 424.0973; calcd for $C_{15}H_{17}AuAuNO$: 424.0970. Elemental analysis: Anal. Calcd for $C_{17}H_{17}AuNO_3F_3$: C, 38.00; H, 3.19; N, 2.61. Found: C, 38.31; H, 3.06; N, 2.64. The sample for the elemental analysis was taken from the bulk material prepared as described above. The batch used for the elemental analysis was obtained in 61% yield.

Preparation of Complex 12. MeOH (10 mL) was added to **1** (103.7 mg, 0.1754 mmol, 1.0 equiv). 2-Methyl-1-butene (20 μL, 0.19 mmol, 1.1 equiv) was added. The flask was sealed with a glass stopper and the reaction mixture was stirred at ambient temperature in the absence of light for 2 d. The volatiles were removed under reduced pressure and the obtained solid was dissolved in CH_2Cl_2 and filtered. The CH_2Cl_2 solution was layered with pentane and left in a refrigerator (ca. 10 °C) overnight furnishing a white precipitate. The solution was collected and filtered, and the volatiles were removed furnishing **12** (44.7 mg, 0.0771 mmol, 44%) as a white, slightly oily, solid. In the elemental analysis of **12**, the %C obtained is outside of the recommended ±0.4% range. ^{1}H NMR (800 MHz, CD_2Cl_2) δ 8.43 (d, 1H, J = 5.3 Hz, H^6), 8.02 (ddd, 1H, J = 8.1, 7.4, 1.5 Hz, H^4), 7.95 (d, 1H, J = 8.1 Hz, H^3), 7.65 (d, 1H, J = 7.8 Hz, $H^{3'}$), 7.61 (s, 1H, $H^{6'}$), 7.48 (ddd, 1H, J = 7.5, 5.4, 0.9 Hz, H^5), 7.21 (d, 1H, J = 7.8 Hz, $H^{4'}$), 3.19 (s, 3H, OCH_3), 2.59 (d, 1H, J = 10.3 Hz, H^a), 2.53 (d, 1H, J = 10.3 Hz, H^a), 2.45 (s, 3H, $ArCH_3$), 1.75 (m, 1H, H^c), 1.70 (m, 1H, H^c), 1.33 (s, 3H, CH_3^e), 0.95 (apparent t, 3H, J = 7.4 Hz, CH_3^d). ^{13}C NMR (201 MHz, CD_2Cl_2) δ 8.6, 22.1, 25.7, 32.9, 43.5, 49.5, 79.2, 118.4 (q, J = 290.2 Hz, OCO$\underline{C}F_3$), 120.1, 124.2, 125.6. 129.0, 134.5, 137.1, 141.0, 141.7, 142.1, 146.3, 160.9, 161.2 (q, J = 36.6 Hz, O$\underline{C}OCF_3$). ^{19}F NMR (188 MHz, CD_2Cl_2) δ −77.1 (OAc^F). MS (ESI, MeOH) m/z (rel. %) 1025 (11), 524 (34), 526 (11), 466 ([M − OAc^F]$^+$, 100), 434 (16). HRMS (ESI, MeOH) found: 466.1440; calcd for $C_{18}H_{23}AuNO$: 466.1440. Elemental analysis: Anal. Calcd for $C_{20}H_{23}AuF_3NO_3$: C, 41.46; H, 4.00; N, 2.42. Found: C, 42.19; H, 3.71; N, 2.14. The sample for the elemental analysis was taken from the bulk material prepared as described above. The batch used for the elemental analysis was obtained in 60% yield.

Preparation of Complex 13. MeOH (10 mL) was added to **1** (100.0 mg, 0.1691 mmol, 1.0 equiv). 2-Methyl-2-butene (50 μL, 0.47 mmol, 2.8 equiv) was added. The flask was sealed with a glass stopper and the reaction mixture was stirred at ambient temperature in the

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absence of light for 2 d. The volatiles were removed under reduced pressure and the obtained solid was dissolved in CH_2Cl_2 and filtered. The CH_2Cl_2 solution was layered with pentane and left in a refrigerator (ca. 10 °C) overnight furnishing a white precipitate. The solution was collected and filtered, and the volatiles were removed furnishing **13** (31.9 mg, 0.0551 mmol, 33%) as a white solid. ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.31 (d, 1H, J = 5.2 Hz, H^6), 8.00 (ddd, 1H, J = 1.5, 7.6, 7.9 Hz, H^4), 7.96 (d, 1H, J = 8.0 Hz, H^3), 7.69 (d, 1H, J = 7.9, $H^{3'}$), 7.54 (s, 1H, $H^{6'}$), 7.45 (ddd, 1H, J = 1.1, 5.6, 7.2 Hz, H^5), 7.21 (d, 1H, J = 7.8 Hz, $H^{4'}$), 3.21 (s, 3H, OCH_3), 2.91 (q, 1H, J = 7.0 Hz, $AuCH^a$), 2.46 (s, 3H, $ArCH_3$), 1.36−1.28 (m, 9H, CH_3^c + CH_3^d + CH_3^e). ^{13}C NMR (201 MHz, CD_2Cl_2) δ 161.2 (q, J = 36.6 Hz, $O\underline{C}OCF_3$), 160.7, 146.6, 141.8, 141.4, 141.3, 138.0, 132.8, 129.0, 125.8, 124.1, 120.1, 118.6 (q, J = 289.5 Hz, $OCO\underline{C}F_3$), 79.1, 62.0, 49.4, 25.7, 24.7, 22.2, 16.7. ^{19}F NMR (188 MHz, CD_2Cl_2) δ −77.3 (OAc^F). MS (ESI, MeOH) m/z (rel. %) 524 (29), 466 ([M − OAc^F]$^+$, 100), 434 (13). HRMS (ESI, MeOH) found: 466.1440; calcd for $C_{18}H_{23}AuNO$: 466.1440. Elemental analysis: Anal. Calcd for $C_{20}H_{23}AuF_3NO_3$: C, 41.46; H, 4.00; N, 2.42. Found: C, 41.69; H, 3.80; N, 2.51. The sample for the elemental analysis was taken from the bulk material prepared as described above. The batch used for the elemental analysis was obtained in 33% yield.

Preparation of Complex 14. Styrene (12 μL, 0.10 mmol, 1.2 equiv) was added to a mixture of **1** (50.0 mg, 0.0846 mmol, 1.0 equiv) in MeOH (3 mL). The reaction mixture was stirred at ambient temperature in the absence of light for 1 d. The volatiles were removed under reduced pressure and the remaining solid was dissolved in CH_2Cl_2 and filtered. The solvent was removed under reduced pressure yielding **14** as a white solid (35.5 mg, 0.0579 mmol, 68%). ^{1}H NMR (800 MHz, CD_2Cl_2) δ 8.44 (ddd, 1H, J = 5.4, 1.6, 0.8 Hz, H^6), 8.03 (ddd, 1H, J = 7.9, 7.6, 1.6 Hz, H^4), 7.94 (d, 1H, J = 8.2 Hz, H^3), 7.64 (d, 1H, J = 7.8 Hz, $H^{3'}$), 7.48 (ddd, 1H, J = 7.4, 5.5, 1.1 Hz, H^5), 7.44 (m, 2H, H^o), 7.36 (m, 2H, H^m), 7.30 (s, 1H, $H^{6'}$), 7.28 (m, 1H, H^p), 7.19 (d, 1H, J = 7.8 Hz, $H^{4'}$), 4.55 (dd, 1H, J = 9.0, 5.1 Hz, H^b), 3.23 (s, 3H, OCH_3), 2.63 (dd, 1H, J = 10.3, 5.1 Hz, H^a), 2.50 (dd, 1H, J = 8.9, 10.2 Hz, H^a), 2.42 (s, 3H, $ArCH_3$). ^{13}C NMR (201 MHz, CD_2Cl_2) δ 161.3 (q, J = 36.7 Hz, $O\underline{C}OCF_3$), 160.9, 146.7, 143.5, 142.4, 141.7, 140.9, 136.7, 132.7, 129.1, 128.8, 127.9, 127.0, 125.7, 124.3, 120.2, 118.4 (q, J = 290.0 Hz, $OCO\underline{C}F_3$), 83.9, 56.8, 41.2, 22.0. ^{19}F NMR (188 MHz, CD_2Cl_2) δ −77.0 (OAc^F). MS (ESI, MeCN) m/z (rel. %) 1113 (100), 1045 (36), 636 ([M + Na]$^+$, 2), 500 ([M − OAc^F]$^+$, 78). HRMS (ESI, MeCN) found: 636.1031; calcd. for $C_{23}H_{21}NO_3F_3AuNa$: 636.1036. Elemental analysis: Anal. Calcd for $C_{23}H_{21}AuF_3NO_3$: C, 45.04; H, 3.45; N, 2.28. Found: C, 45.06; H, 3.44; N, 2.30. The sample for the elemental analysis was taken from the bulk material prepared as described above. The batch used for the elemental analysis was obtained in 72% yield.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00218.

Complete experimental procedures, MS and NMR data are given for all new complexes; Crystallographic methods and crystallographic data for complexes **4b**, **5a**,**b**, **6**, **8**, and **13**−**16** are given together with elemental analyses for selected complexes (PDF)

Accession Codes

CCDC 1835274−1835282 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896−7936.

(2) Hashmi, A. S. K. *Chem. Rev.* **2007**, *107*, 3180−3211.

(3) Chiarucci, M.; Bandini, M. *Beilstein J. Org. Chem.* **2013**, *9*, 2586−2614.

(4) Dorel, R.; Echavarren, A. M. *Chem. Rev.* **2015**, *115*, 9028−9072.

(5) Corma, A.; Leyva-Pérez, A.; Sabater, M. J. *Chem. Rev.* **2011**, *111*, 1657−1712.

(6) Krause, N.; Winter, C. *Chem. Rev.* **2011**, *111*, 1994−2009.

(7) Li, Z.; Brouwer, C.; He, C. *Chem. Rev.* **2008**, *108*, 3239−3265.

(8) *Modern Gold Catalyzed Synthesis*; Hashmi, A. S. K., Toste, F. D., Eds.; Wiley-VCH: Weinheim, 2012.

(9) Schmidbaur, H.; Schier, A. *Organometallics* **2010**, *29*, 2−23.

(10) Balcells, D.; Eisenstein, O.; Tilset, M.; Nova, A. *Dalton Trans.* **2016**, *45*, 5504−5513.

(11) Brooner, R. E. M.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 11714−11724.

(12) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *446*, 395−403.

(13) Rezsnyak, C. E.; Autschbach, J.; Atwood, J. D.; Moncho, S. *J. Coord. Chem.* **2013**, *66*, 1153−1165.

(14) Savjani, N.; Roşca, D.-A.; Schormann, M.; Bochmann, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 874−877.

(15) Rekhroukh, F.; Brousses, R.; Amgoune, A.; Bourissou, D. *Angew. Chem., Int. Ed.* **2015**, *54*, 1266−1269.

(16) Rekhroukh, F.; Estevez, L.; Bijani, C.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Organometallics* **2016**, *35*, 995−1001.

(17) Rekhroukh, F.; Blons, C.; Estevez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *Chem. Sci.* **2017**, *8*, 4539−4545.

(18) Rekhroukh, F.; Estevez, L.; Mallet-Ladeira, S.; Miqueu, K.; Amgoune, A.; Bourissou, D. *J. Am. Chem. Soc.* **2016**, *138*, 11920−11929.

(19) Serra, J.; Font, P.; Sosa Carrizo, E. D.; Mallet-Ladeira, S.; Massou, S.; Parella, T.; Miqueu, K.; Amgoune, A.; Ribas, X.; Bourissou, D. *Chem. Sci.* **2018**, *9*, 3932−3940.

(20) Harper, M. J.; Emmett, E. J.; Bower, J. F.; Russell, C. A. *J. Am. Chem. Soc.* **2017**, *139*, 12386−12389.

DOI: 10.1021/acs.organomet.8b00218
Organometallics XXXX, XXX, XXX−XXX

(21) Langseth, E.; Nova, A.; Tråseth, E. A.; Rise, F.; Øien, S.; Heyn, R. H.; Tilset, M. *J. Am. Chem. Soc.* **2014**, *136*, 10104−10115.
(22) Holmsen, M. S. M.; Nova, A.; Balcells, D.; Langseth, E.; Øien-Ødegaard, S.; Heyn, R. H.; Tilset, M.; Laurenczy, G. *ACS Catal.* **2017**, *7*, 5023−5034.
(23) Langseth, E.; Görbitz, C. H.; Heyn, R. H.; Tilset, M. *Organometallics* **2012**, *31*, 6567−6571.
(24) Holmsen, M. S. M.; Nova, A.; Balcells, D.; Langseth, E.; Øien-Ødegaard, S.; Tråseth, E. A.; Heyn, R. H.; Tilset, M. *Dalton Trans.* **2016**, *45*, 14719−14724.
(25) Langseth, E.; Scheuermann, M. L.; Balcells, D.; Kaminsky, W.; Goldberg, K. I.; Eisenstein, O.; Heyn, R. H.; Tilset, M. *Angew. Chem., Int. Ed.* **2013**, *52*, 1660−1663.

DOI: 10.1021/acs.organomet.8b00218
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