Synthesis, Structure, and Reactivity of Gold(I) α-Oxo Carbenoid Complexes

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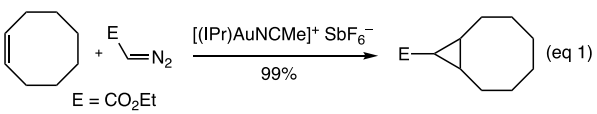
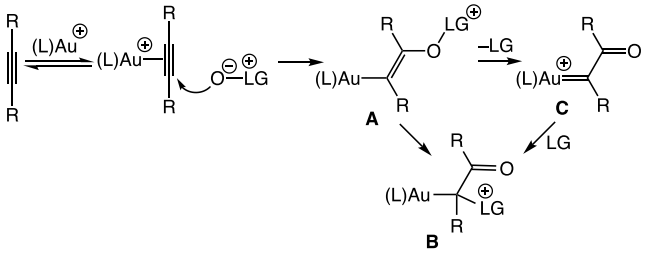
ABSTRACT: The α-trifluoromethanesulfonyl α-oxo carbenoid complexes (IPr)AuCH(OTf)COR [R = OEt (**1a**), *p*-tolyl (**1b**)] were isolated from reaction of (IPr)Au(OTf) with the corresponding α-diazo carbonyl compound. The α-pyridinium, α-oxo carbenoid complexes $[(IPr)AuCH(4\text{-}C_5H_4NMe)COR]^+$ OTf^- (**2**), the α-sulfonium, α-oxo carbenoid complexes $[(IPr)AuCH(SR'_2)COR]^+$ OTf^- [**3** (R' = Me), **4** (R' = Ph)] and the α,α-dioxo carbenoid complexes $[(IPr)AuC(R)(CO_2Me)_2]^+$ OTf^- [R = 4-C_5H_4NMe (**5**), R = SPh_2 (**6**)] were synthesized either via reaction of complexes **1** with 4-picoline or dimethyl sulfide or via reaction of (IPr)Au(OTf) with stabilized ylide. Complexes **1** – **6** were thermally stable and characterized in solution and in the case of complexes **2** and **3**, by single crystal X-ray diffraction. Complex **1b** underwent carbene transfer to cyclohexene in modest yield at 75 °C. The α-pyridinium- and α-sulfonium α-oxo carbenoid complexes **2** and **3** displayed no reactivity toward dimethyl sulfide, 4-picoline, 1-octyne, or *p*-methoxystyrene. Complex **5** underwent rapid displacement of the ylide ligand in the presence of dimethyl sulfide or 4-picoline. Taken together, we obtained no evidence suggesting that these α-sulfonium or α-pyridinium α-oxo carbenoid complexes might behave as α-oxo carbene surrogates.

INTRODUCTION

Over the past decade, cationic gold(I) complexes have emerged as versatile catalysts for the functionalization of C–C multiple bonds.[1] In addition to these π-activation processes, a diverse range of gold-catalyzed transformations have been developed that are thought to proceed via cationic, two-coordinate gold carbene or carbenoid intermediates,[1] and considerable effort has been directed toward understanding the structure and reactivity of these complexes.[2] An important subset of these cationic intermediates are gold α-oxo carbene or carbenoid complexes generated via decomposition of an α-diazo carbonyl compound (eq 1)[3] or, more conveniently, from the oxidation of alkynes with pyridinum *N*-oxides, sulfoxides, and related reagents.[4-8] These α-oxo carbene/carbenoid intermediates engage in a range of transformations including alkene and alkyne cyclopropanation, carbene-carbene cross coupling, C–H and X–H insertion, and cycloaddition.[3-8]



Although the gold-catalyzed decomposition of α-diazo carbonyl compounds and the gold-catalyzed oxidation of alkynes are often assumed to proceed via discrete gold α-oxo carbene intermediates, there is no direct evidence for the existence of the free two-coordinate carbene complex[9,10] and rather, computational[11-13] and experimental[14,15] evidence suggests that an α-oxo carbenoid complex, rather than a free α-oxocarbene, might be the reactive species, at least under certain conditions. For example, Pérez has shown that the rate of N_2 evolution in the cyclopropanation of styrene with ethyl diazoacetate catalyzed by a mixture of (IPr)AuCl and NaBArF {BArF = B[3,5-$C_6H_3(CF_3)_2]_4$} displayed linear dependence on [styrene],[11] which is inconsistent with rate-limiting N_2 dissociation from $[(IPr)AuC(H)(CO_2Et)(N_2)]^+$. Similarly, tandem mass spectrometry/ion spectroscopy analysis of the reactions of alkynes with pyridine *N*-oxide and $(IPr)Au^+$ suggest that the initially formed *N*-alkenoxypyridinium complex **A** undergoes intramolecular rearrangement to form the gold(I) α-pyridinium,α-oxo carbenenoid complex **B**, which can alternatively be viewed as a gold complex bearing a carbonyl stabilized pyridinium ylide, without the intermediacy of the α-oxo carbene complex **C** (Scheme 1).[15] These observations suggest the possible involvement of either **A** or **B** as the reactive species in the gold-catalyzed oxidation of alkynes with pyridine *N*-oxides.



Scheme 1. Potential intermediates in the gold(I)-catalyzed oxidation of alkynes with pyridine *N*-oxides (O–LG).

Owing to safety and practicality issues associated with employment of α-diazo carbonyl compounds on large scale,

there has been longstanding interest in the use of carbonyl-stabilized sulfonium ylide compounds as surrogates for α-diazo carbonyl compounds in transition metal-catalyzed transformations.[16] Included in this body of work are gold-catalyzed cycloaddition,[17,18] cyclopropanation,[19-23] and N–H activation[24] processes employing carbonyl-stabilized sulfonium ylides. Both inner-sphere and outer-sphere pathways have been proposed for these transformations which may likewise involve gold α-oxo carbene or carbenoid intermediates.[17-24] In any event, the potentially strong ligating abilities of a stabilized sulfonium ylide suggests the potential involvement of gold sulfonium ylide complexes as on-cycle or off-cycle intermediates in these transformations.

The observations outlined in the preceding paragraphs raise questions regarding the potential involvement of gold α-oxo carbenoid complexes in a number of gold-catalyzed transformations. Indeed, a handful of gold carbenoid complexes have recently been shown to function as gold carbene precursors or surrogates.[25-31] Chen has shown that gold phosphonium benzylide complexes **D** generate reactive gold benzylidene complexes in the gas phase,[26] and we have recently shown that sulfonium benzylide complexes **E** generate gold benzylidene complexes in solution under mild conditions (Chart 1).[27] Chen has similarly shown that the gold SO_2-imidazolium complex **F** generates reactive gold arylidene complexes in solution.[28] Echavarren and Fürstner have independently reported thermally unstable α-(triflouromethanesulfonyl)methyl carbenoid complex **G** and α-(triflouromethanesulfonyl)difluromethyl carbenoid complex **H**, respectively, which undergo gold to alkene carbene transfer at or below room temperature.[29-31]

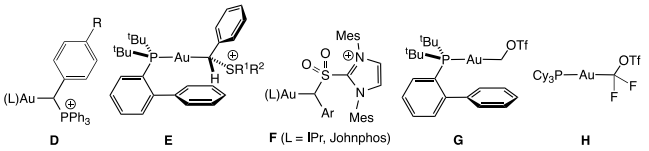
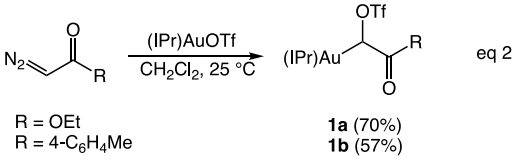


Chart 1. Reactive gold carbenoid complexes.

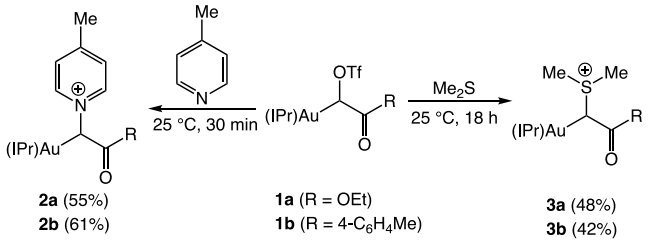
In comparison to gold benzyl and methyl carbenoid complexes, the structures and reactivity of gold α-oxo carbenoid complexes remains largely unexplored and, as such, the potential for these complexes to serve as precursors or surrogates to gold α-oxo carbene complexes has not been evaluated. Although gold α-oxo carbenoid complexes bearing an α-phosphonium group are known,[32] the structures and reactivity of these complexes have not been extensively explored nor is it likely that these compounds display significant reactivity owing to the high stability of phosphonium ylide ligand.[33] Therefore, to gain insight into the potential role of gold α-oxo carbenoid complexes in gold(I) catalysis, we have investigated the synthesis, structure, and reactivity of gold α-oxo carbenoid complexes bearing an α-pyridinium, α-sulfonium, or α-trifluromethanesulfonyl group.

RESULTS

Gold α-trifluoromethanesulfonyl, α-oxo carbenoid complexes. As an entry point to the synthesis of gold α-oxo carbenoid complexes, we targeted the synthesis of gold α-trifluoromethanesulfonyl α-oxo carbenoid complexes via reaction of (IPr)Au(OTf) with α-diazo carbonyl compounds, which was modeled after Echavarren's synthesis of gold halomethyl carbenoid complexes.[29] To this end, treatment of (IPr)Au(OTf) with ethyl diazoacetate in CH_2Cl_2 at room temperature for 30 min followed by crystallization from CH_2Cl_2/pentane led to isolation of the gold α-trifluoromethanesulfonyl ester enolate complex (IPr)AuCH(OTf)CO_2Et (**1a**) in 70% yield. In a similar manner, the gold α-trifluoromethanesulfonyl ketone enolate complex (IPr)AuCH(OTf)C(O)(4-C_6H_4Me) (**1b**) was isolated in 57% yield from the reaction of (IPr)Au(OTf) with *p*-methyl-2-diazoacetophenone (eq 2). In contrast to the α-(triflouromethanesulfonyl) carbenoid complexes **G** and **H**, complexes **1** were stable for hours in solution at room temperature and were characterized in solution by NMR spectroscopy and by mass spectrometry. For example, the ^{1}H NMR spectra of complexes **1** displayed a diagnostic one-proton singlet at δ 5.27 (**1a**) and 6.31 (**1b**) assigned to the α proton and the ^{13}C NMR spectra displayed a resonance at δ 96.2 (**1a**) and 104.0 (**1b**) assigned to the α carbon atom. The IR spectra of complexes **1** displayed a strong C=O stretching band at 1723 (**1a**) and 1669 (**1b**) cm^{-1}, which established the presence of a carbon-bound enolate ligand.



Gold α-pyridinium and α-sulfonium α-oxo carbenoid complexes. The α-trifluromethanesulfonyl enolate complexes **1a** and **1b** reacted cleanly with 4-picoline within 30 min at room temperature to form the α-pyridinium, α-oxo carbenoid complexes [(IPr)AuCH(4-C_5H_4NMe)CO_2Et]$^+$ OTf$^-$ (**2a**) and [(IPr)AuCH(4-picoline)C(O)(4-C_6H_4Me)]$^+$ OTf$^-$ (**2b**), which were isolated in 55-61% yield as colorless crystals from CH_2Cl_2/pentane (Scheme 2). In a similar manner, complexes **1a** and **1b** reacted with dimethyl sulfide at room temperature over 18 h to form the α-dimethylsulfonium α-oxo carbenoid complexes [(IPr)AuCH(SMe_2)CO_2Et]$^+$ OTf$^-$ (**3a**) and [(IPr)AuCH(SMe_2)C(O)(4-C_6H_4Me)]$^+$ OTf$^-$ (**3b**), respectively, which were isolated as colorless crystals in 42-48% yield (Scheme 2).



Scheme 2. Reaction of 4-picoline and dimethyl sulfide with complexes **1.**

To probe the mechanism of the nucleophilic displacement of the trifluromethanesulfonyl group in the conversion of complexes **1** to **2** and **3**, we analyzed the kinetics of the conversion of **1a** to **2a**. To this end, an equimolar mixture of **1a** (4.0 mM) and 4-picoline (4.1 mM) in CD_2Cl_2 at 25 °C was monitored periodically by ^{1}H NMR spectroscopy. A plot of 1/[**1a**] versus time was linear to >3 half-lives with a second-order rate constant of k = 2.30 ± 0.05 M^{-1} s^{-1} (Figure 1). The

second-order behavior is consistent with a bimolecular pathway for the conversion of **1a** and 4-picoline to **2a**, presumably via direct S_N2 displacement of the α-trifluoromethanesulfonyl group by 4-picoline.

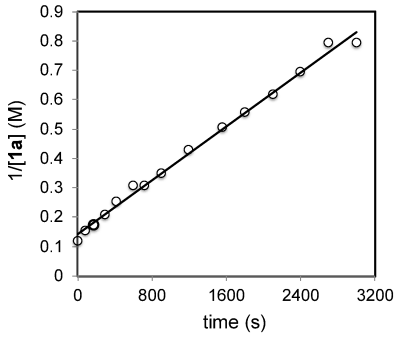
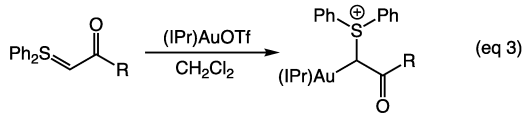


Figure 1. Second-order plot for the reaction of **1a** (4.0 mM) with 4-picoline (4.1 mM) in CD_2Cl_2 at 25 °C.

Attempted synthesis of the α-diphenylsulfonium α-oxo carbenoid complex $[(IPr)AuCH(SPh_2)(CO_2Et)]^+$ OTf^- (**4a**) via reaction of α-trifluromethanesulfonyl carbenoid complex **1a** with diphenyl sulfide proved unsuccessful, presumably due to the lower nucleophilicity of diphenyl sulfide relative to 4-picoline or dimethyl sulfide. Rather, complex **4a** was isolated as colorless crystals in 85% yield from the direct reaction of the sulfonium ylide Ph_2SCHCO_2Et with (IPr)Au(OTf) at room temperature for 15 min (eq 3). In a similar manner, the corresponding α-diphenylsulfonium phenacyl complex $[(IPr)AuCH(SPh_2)C(O)(4\text{-}C_6H_4Me)]^+$ OTf^- (**4b**) was isolated as a white solid in 48% yield from reaction of $Ph_2SCHCO(4\text{-}C_6H_4Me)$ with (IPr)Au(OTf) at 0 °C (eq 3).



R = OEt
R = 4-C_6H_4Me

4a (85%)
4b (49%)

The α-pyridinium carbenoid complexes **2** and the α-sulfonium carbenoid complexes **3** and **4** were thermally stable and were characterized in solution and, in the cases of **2** and **3**, in the solid state. In the ^1H NMR spectra of complexes **2** - **4**, as was the case with α-trifluromethanesulfonyl complexes **1**, particularly diagnostic was the α proton resonance in the ^1H NMR spectrum, which ranged from δ 3.41 (**3a**) to 6.10 (**2b**) and the α carbon resonance in the ^{13}C NMR spectra, which ranged from δ 61.1 for (**3a**) to δ 84.2 for (**2b**). Similarly, the presence of a stereogenic α-carbon atom in complexes **2** - **4** was established by the presence of four sets of doublets in the range δ 1.25 – 0.80 corresponding to the diastereotopic IPr methyl groups.

The molecular structures of gold α-oxo carbenoid complexes **2a**, **2b**, **3a**, and **3b** were determined by single crystal X-ray diffraction (Figure 2, Table 1). In the solid state, the gold atom of these carbenoid complexes adopts a linear conformation with C–Au–C angles ranging from 174.5 – 179 °. The gold–carbenoid bond (Au–C28) is 0.065 – 0.084 Å longer than is the gold-IPr (Au–C1) bond with the ketone complexes **2b** and **3b** having a nominally larger difference in the Au–C1/Au–C28 bond distances than do the corresponding ester complexes **2a** and **3a**. The carbenoid ligand of complexes **2** and **3** is oriented with a *syn*-periplanar arrangement of the α-heteroatom group and the carbonyl oxygen atom, with O–C–C–X (X = N,S) dihedral angles ranging from 11.7° for **3b** to 27.4° for **3a**. The gold-bound carbon atom of the carbenoid ligand of complexes **2** and **3** adopts a distorted sp^3 geometry with two smaller angles (106-108°) and one larger angle (111 – 116 °), with the ester derivatives **2a** and **3a** displaying the largest deviations between large and small angles. For complexes **2a**, **2b**, and **3b**, the Au–C28–S/N3 is the larger angle whereas in the case of **3a**, the C29–C28–S is the larger angle.

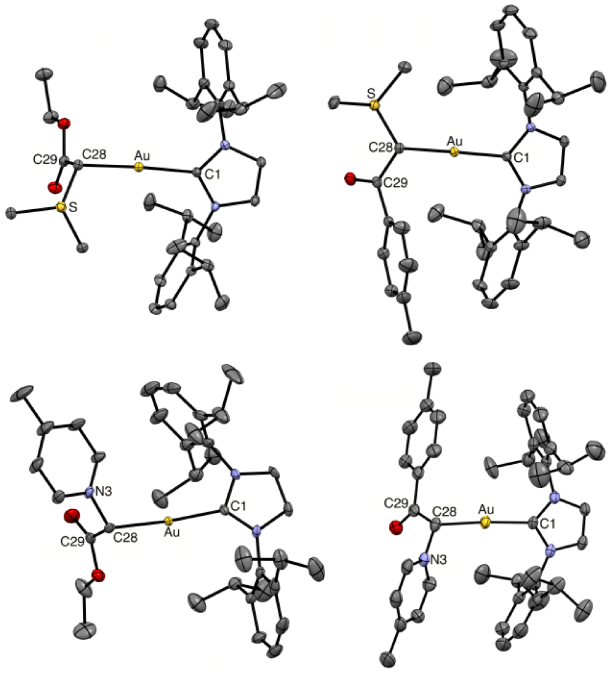


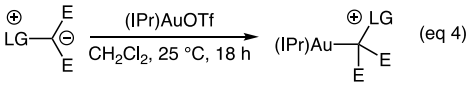
Figure 2. ORTEP diagrams of complexes **2a** (lower left), **2b** (lower right), **3a** (upper left), and **3b** (upper right) with ellipsoids shown at the 50% probability level and with counterion, solvent, and hydrogen atoms omitted for clarity.

Table 1. Selected bond lengths (Å), bond angles (deg), and dihedral angles (deg) for complexes **2a**, **2b**, **3a**, and **3b**.

	2a	**2b**	**3a**	**3b**
Au–C1	2.016(5)	2.013(3)	2.012(3)	2.005(1)
Au–C28	2.081(5)	2.087(3)	2.088(4)	2.084(1)
C28–S/N3	1.491(8)	1.484(4)	1.782(4)	1.785(1)
C28–C29	1.501(9)	1.491(4)	1.492(5)	1.486(2)
C1–Au–C28	174.4(2)	176.9(1)	175.4(1)	179.01(5)
Au–C28–S/N3	115.3(4)	112.6(2)	108.7(2)	111.27(6)
Au–C28–C29	106.5(4)	104.7(2)	106.5(2)	106.15(8)
S/N3–C28–C29	105.9(5)	110.0(2)	114.9(3)	107.95(9)

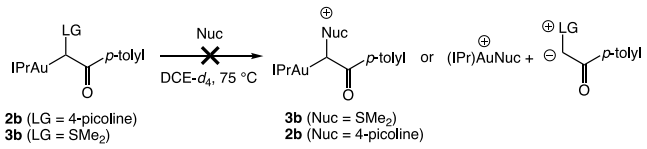
S/N3–C28–C29–O1	20.5(9)	14.6(4)	27.4(5)	11.7(2)

α,α-Dioxo carbenoid complexes. We also sought to synthesize α-pyridinium and α-sulfonium α,α-dioxo carbenoid complexes from which, comparisons could be drawn regarding stability and/or reactivity to α-oxo carbenoid complexes **2** – **4**. To this end, treatment of (IPr)Au(OTf) with 4-picolinium bis(carbomethoxy)methylide in CH_2Cl_2 at room temperature led to isolation of [(IPr)AuC(4-C_5H_4NMe)(CO_2Me)$_2$]$^+$ OTf^- (**5**) in 70% yield (eq 4). Similarly, reaction of (IPr)Au(OTf) with diphenylsulfoxonium bis(carbomethoxy)methylide led to isolation of [(IPr)AuC(SPh_2)(CO_2Me)$_2$]$^+$ OTf^- (**6**) in 39%. Formation of complexes **5** and **6** was established by the ~0.3 ppm upfield shift of the methoxy resonances of complexes **5** and **6** relative to the free methylide.



E = CO_2Me, LG = 4-picoline — **5** (70%)
E = CO_2Me, LG = SPh_2 — **6** (39%)

Reactions of carbenoid complexes with neutral two-electron donors. As noted above, the α-trifluoromethanesulfonyl group of complexes **1** was readily displaced by 4-picoline or dimethylsulfide to form α-pyridinium and α-sulfonium α-oxo carbenoid complexes **2** and **3** (eq 2). In contrast, complexes **2** and **3** displayed no reactivity toward 4-picoline or dimethylsulfide. For example, treatment of α-pyridinium α-oxo carbenoid complex **2b** with excess dimethyl sulfide in DCE-d_4 at 75°C for 9 h led neither to Cα–N bond cleavage to form α-sulfonium complex **3b** nor to Au–C bond cleavage to form the free pyridinium ylide (4-C_5H_4NMe)CHCO(4-C_6H_4Me) and (IPr)AuSMe_2 (Scheme 3). Similarly, heating a solution of α-sulfonium α-oxo carbenoid complex **3b** with excess 4-picoline led to no detectable Cα–S or Au–C bond cleavage. Complex **3b** likewise failed to react with pyridinium ylide (4-C_5H_4NMe)CHCO(4-C_6H_4Me) at 75 °C.

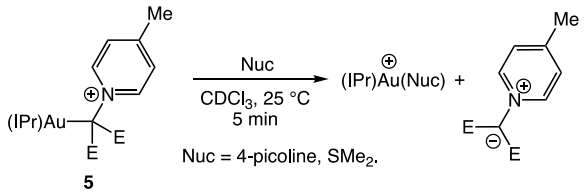


2b (LG = 4-picoline)
3b (LG = SMe_2)

3b (Nuc = SMe_2)
2b (Nuc = 4-picoline)

Scheme 3. Stability of complexes **2** and **3** toward nucleophiles.

In contrast to the α-oxo carbenoid complexes **2** and **3**, the α,α-dioxo carbenoid complex **5** underwent facile ligand displacement with 4-picoline and dimethylsulfide. For example, treatment of **5** with excess 4-picoline at room temperature resulted in immediate (≤ 5 min) displacement of 4-picolinium bis(carbomethoxy)methylide to form the gold picoline complex [(IPr)Au(4-C_5H_4NMe)]$^+$ OTf^-[34] and free ylide (Scheme 4). Similarly, treatment of **5** with excess dimethyl sulfide led to immediate formation of the gold sulfide complex [(IPr)Au(SMe_2)]$^+$ OTf^- and free methylide (Scheme 4).



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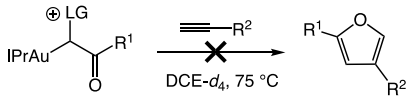
Scheme 4. Displacement of methylide from complex **5**.

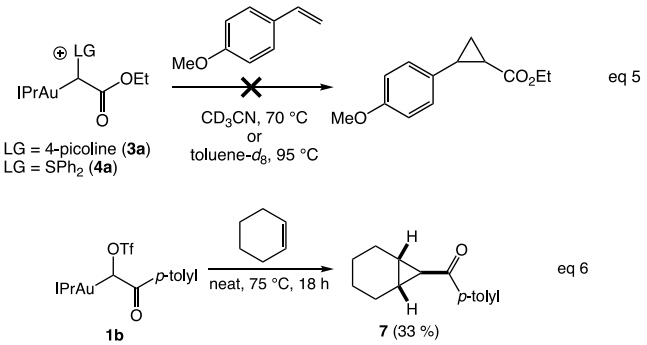
Reactions of α-oxo carbenoid complexes with C–C multiple bonds. Skrydstrup and Maulide have described the gold(I)-catalyzed annulation of terminal alkynes with stabilized sulfonium ylides to form furans, which was proposed to occur via outer-sphere addition of ylide on a gold π-alkyne complex, presumably formed in competitive equilibrium with the σ-sulfonium ylide complex.[17,18] To evaluate whether α-sulfonium or α-pyridinium α-oxo carbenoid complexes were viable intermediates in furan formation, we investigated the reactions of α-oxo carbenoid complexes **2b, 3a**, and **3b** with terminal alkynes in DCE-d_4 at 75 °C (Scheme 5). However, as is shown in Table 2, various combinations of leaving group (LG), carbonyl substituent (R^1), and alkyne substituent (R^2) led to no detectable consumption of carbenoid complex and no detectable formation of furan.



LG	complex	R^1	R^2
SMe_2	**3b**	*p*-tolyl	*n*-hexyl
SMe_2	**3b**	*p*-tolyl	*t*-butyl
SMe_2	**3b**	*p*-tolyl	*p*-tolyl
SMe_2	**3a**	OEt	*n*-hexyl
4-picoline	**2b**	*p*-tolyl	*n*-hexyl

Scheme 5. Attempted reactions of α-oxo carbenoid complexes **2** and **3** with terminal alkynes.

We likewise evaluated the potential of gold carbenoid complexes to engage in gold to alkene carbene transfer. Treatment of the α-sulfonium or α-pyridinium α-oxo carbenoid complexes **3a** and **4a** with excess 4-methoxystyrene in either CD_3CN at 70 °C or toluene-d_8 at 95 °C led to no detectable consumption of carbenoid complex or formation of cyclopropane after 9 h (eq 5). In comparison, heating a suspension of the α-trifluoromethanesulfonate α-oxo carbenoid complex **1b** in neat cyclohexene at 75 °C for 18 h led to complete consumption of **1b** to form the bicyclo[4.1.0]heptane derivative **7** in 33% yield (^{1}H NMR) and (IPr)Au(OTf), which precipitated from solution (eq 6).[35,36] In an effort to increase the efficiency of gold to carbene alkene transfer from **1b**, we likewise investigated the Lewis acid-promoted ionization of **1b** in cyclohexene. However, slowly warming a solution of **1b** and $SbCl_5$ in cyclohexene from –78 °C to room temperature over the course of 4 h led to complete consumption of **1b** to form (IPr)AuCl without detectable formation of **7** or 1,4-di-*p*-tolylbut-2-ene-1,4-dione.[36]

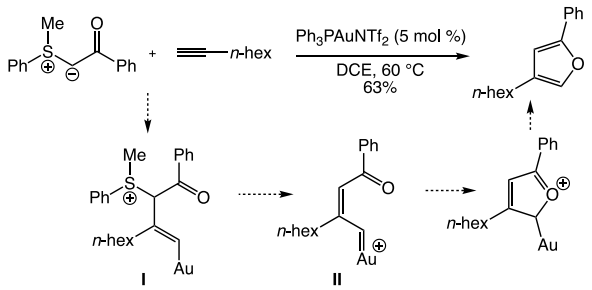


DISCUSSION

The studies described above provide some insights into the potential roles of α-oxo carbenoid complexes in gold-catalyzed transformations. Firstly, the stability of the α-sulfonium- and α-pyridinium α-oxo carbenoid complexes with respect to ligand displacement and the absence of gold to alkene carbene transfer behavior argue strongly against the participation of these complexes in the gold-catalyzed reactions of alkynes with pyridine *N*-oxides, sulfoxides, and related reagents.[4-8] However, these results do not rule out gold *N*-alkenoxypyridinium complexes (**A**, Scheme 1) and their variants as the reactive species generated in gold-catalyzed alkyne oxidation reactions. Here it should be noted that Bourissou has characterized a three-coordinate gold α-oxo carbene complex and established this species as a viable intermediate in the carbene transfer reactions of α-diazo carbonyl reactions catalyzed by three-coordinate gold bis(phosphine) complexes.[9] Likewise, Hofmann has validated a three-coordinate copper α-oxo carbene complex in the analogous copper-catalyzed process.[10] However, because three-coordinate gold and copper carbene complexes are significantly more stable than are cationic two-coordinate gold carbene complexes,[2,37] the relevance of these observations to the behavior of cationic two-coordinate gold complexes is not clear.

The gold α-trifluoromethanesulfonyl α-oxo carbene complexes **1** are significantly more stable than are the α-(triflouromethanesulfonyl) carbenoid complexes **G** and **H** reported by Echavarren and Fürstner, respectively.[29,30] Nevertheless, the slow gold to alkene carbene transfer from complex **1b** to cyclohexene is in line with the observations of Echavarren and Fürstner, who showed that complexes **G** and **H** engage readily in gold to alkene carbene transfer.[29,30] Importantly, DFT calculations and kinetic analysis of gold to alkene carbene transfer from α-(trifluoromethanesulfonyl)methyl carbenoid complexes supported a mechanism involving direct displacement of the trifluoromethanesulfonyl group by the alkene without formation of the free gold methylidene complex.[29]

The results described herein also provide some insight into the mechanisms of the gold-catalyzed cycloaddition and cyclopropanation of alkenes and alkynes with stabilized sulfonium ylides.[17-23] For example, Maulide has reported a range of gold-catalyzed cycloaddition and cyclopropanation processes employing sulfonium ylides derived from malonates and β-keto esters.[18-23] Computational analysis of these transformations support pathways involving outer-sphere addition of the sulfonium ylide on a gold π-alkene, π-alkyne, or π-allene complex, as opposed to inner-sphere pathways involving α-oxo carbene intermediates or α-sulfonium α-oxo carbenoid intermediates.[18-23] In comparison, Skrydstrup has described the gold(I)-catalyzed annulation of terminal alkynes with ketone-stabilized sulfonium ylides to form furans, which was proposed to occur via outer-sphere addition of ylide on a gold π-alkyne to form sulfonium intermediate **I** followed by expulsion of sulfide and subsequent attack of ketone oxygen atom on the α carbon atom of the resulting vinylogous oxo carbene intermediate **II** (Scheme 6).[17]



Scheme 6. Proposed mechanism for the gold-catalyzed annulation of stabilized sulfonium ylide with 1-octyne.[17]

Our observations inform on the feasibility of the mechanism depicted in Scheme 6. Firstly, the resistance of α-sulfonium, α-oxo carbenoid complexes **3** and **4** toward loss of sulfide either spontaneously or via nucleophilic displacement argues against the formation of the vinylogous oxo carbene intermediate **II** and points to the direct attack of the ketone oxygen atom on the C1 atom of intermediate **I**, as was proposed by Maulide.[18] Secondly, the proposed outer-sphere mechanism requires formation of a π-alkyne complex in the presence of the sulfonium ylide. However, the failure of 4-picoline, which is much stronger ligand for gold than is the alkyne,[34,38] to displace the sulfonium ylide from the α-sulfonium α-oxo carbenoid complex **3a** and the failure of **3a** to react with 1-octyne causes us to question the feasibility of alkyne complexation in the presence of a ketone-stabilized sulfonium ylide. In comparison, the transformations reported by Maulide employ sulfonium ylides derived from malonates and β-keto esters.[18-23] Here, the facile displacement of the pyridinium ylide ligand from the α-pyridinium, α-oxo carbenoid complex **5** (Scheme 4) supports the feasibility of alkyne, alkene, or allene complexation to gold in the presence of a sulfonium ylide derived from a malonate or β-keto ester.

CONCLUSIONS

We have synthesized several families of gold α-oxo carbenoid complexes including α-trifluoromethanesulfonyl (**1**), α-pyridinium (**2**), and α-sulfonium (**3**, **4**) α-oxo carbenoid complexes and α,α-dioxo carbenoid complexes (**5**,**6**), all of which were stable at room temperature in solution and in the solid state. The stability of these α-oxo carbenoid complexes with respect to displacement of the α-leaving group or the ylide ligand varied significantly. For example, the triflate group of the gold α-(trifluoromethanesulfonyl) α-oxo carbenoid complexes **1** was readily displaced in an S_N2 process by 4-picoline or dimethyl sulfide, whereas the methylide ligand of the α,α-dioxo carbenoid complex **5** was readily

displaced by these same neutral two-electron donors. In contrast, the gold α-pyridinium and α-sulfonium α-oxo carbenoid complexes **2**-**4** displayed no reactivity toward neutral two electron donors.

The gold α-trifluoromethanesulfonyl α-oxo carbene complex **1b** underwent gold to alkene carbene transfer to cyclohexene at 75 °C, albeit slowly and in modest yield, whereas gold α-sulfonium- and α-pyridinium α-oxo carbenoid complexes displayed no reactivity toward terminal alkynes or *p*-methoxystyrene. An intriguing, but as yet unresolved question raised from these studies relates to the reactive intermediate generated in the gold-catalyzed oxidation of alkenes with pyridine *N*-oxides, sulfoxides, and related reagents.[4-8] The stability of the gold α-pyridinium α-oxo carbenoid complexes **2** argues strongly against the participation of these compounds and their variants in gold-catalyzed alkyne oxidation processes. Similarly, the mass spectrometry studies of Roithová argued against the involment of the free gold α-oxo carbene complex in these transformations.[15] These observations suggest the involvement of an *N*-alkenoxypyridinium complex as the reactive intermediate in these transformations, as has likewise been suggested by Gagosz,[39] but this hypothesis remains to be experimentally verified.

EXPERIMENTAL SECTION

General Methods. Reactions were run under a nitrogen atmosphere in flame dried glassware using standard glovebox and Schlenk techniques. NMR Spectra were obtained on a 400 MHz Varian Inova spectrometer and a 500 MHz Bruker spectrophotometer. ^{13}C NMR spectra were referenced to residual $CDCl_3$ (δ 77.2) or CH_2Cl_2 (δ 53.8). The ^1H NMR spectra was referenced to residual $CDCl_3$ (δ 7.26) or CH_2Cl_2 (δ 5.32). Infrared (IR) spectra were obtained on a Nicolet 380 FT-IR at 25 °C. Diethyl ether, CH_2Cl_2, and THF were purified by passage through columns of activated alumina under nitrogen. Silver-free (IPr)Au(OTf) was synthesized employing published procedures.[40] *p*-Methyl-2-diazoacetophenone,[41] Ph_2SCHCO_2Et,[42] $Ph_2SCHC(O)(4\text{-}C_6H_4Me)$,[42] diphenylsulfonium bis(carbomethoxy)methylide,[21] and 4-picolinium bis(carbomethoxy)methylide[43] were synthesized employing known procedures. All other reagents were obtained through major chemical suppliers and used as received.

Gold Carbenoid Complexes

(IPr)AuCH(OTf)CO$_2$Et (1a). Ethyl diazoacetate (8.6 μL, 8.2 × 10^{-2} mmol) was added dropwise to a solution of (IPr)Au(OTf) (60 mg, 8.2 × 10^{-2} mmol) in CH_2Cl_2 (5 mL) under nitrogen at 25 °C and the resulting solution was stirred for 30 min and then concentrated under vacuum. Vapor diffusion of pentane into a concentrated CH_2Cl_2 solution at 4 °C formed white crystals that were rinsed with hexanes and dried under vacuum to give **1a** (47 mg, 70%). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.53 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 4H), 7.22 (d, *J* = 0.9 Hz, 2H), 5.27 (s, 1H), 3.87 (dq, *J* = 10.7, 7.1 Hz, 1H), 3.78 (dq, *J* = 10.7, 7.2 Hz, 1H), 2.54 (sept, *J* = 6.8 Hz, 2H), 2.51 (sept, *J* = 6.8 Hz, 2H), 1.29 (d, *J* = 6.9 Hz, 12H), 1.22 (d, *J* = 6.9 Hz, 12H), 0.97 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 188.2, 174.3, 145.8, 133.9, 130.5, 124.0, 123.4, 96.2, 59.6, 28.7, 24.1, 24.1, 23.6, 14.0. ^{19}F NMR (376 MHz, CD_2Cl_2): δ −76.57. IR (CH_2Cl_2): 1723 cm^{-1} ($\nu_{C=O}$). HRMS (ESI) calcd. (found) for $C_{32}H_{42}AuN_2O_5S$ (MH^+): 764.3485 (764.3496).

(IPr)AuCH(OTf)C(O)(4-C$_6$H$_4$Me) (1b). A solution of *p*-methyl-2-diazoacetophenone (33.5 mg, 0.209 mmol) in benzene (2 mL) was added dropwise to a solution of (IPr)Au(OTf) (102.5 mg, 0.139 mmol) in benzene (2 mL) and stirred for 30 min at room temperature, during which time nitrogen evolution was observed and (IPr)Au(OTf) dissolved to afford a homogenous solution. The solution was then cooled at −20 °C until frozen and then thawed forming a white precipitate. The solution phase was decanted and the precipitate was rinsed with hexanes and dried under vacuum to give **1b** (23 mg, 57%) as a white solid. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.50 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.34 (m, 4H), 7.30 – 7.26 (m, 4H), 7.25 – 7.20 (m, 4H), 7.19 (s, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.31 (s, 1H), 2.46 (sept, *J* = 6.8 Hz, 2H), 2.45 (sept, *J* = 6.8 Hz, 2H), 2.37 (s, 3H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.19 (d, *J* = 6.9 Hz, 6H), 1.17 (d, *J* = 6.9 Hz, 6H), 1.11 (d, *J* = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 194.8, 188.3, 146.0, 142.1, 134.2, 133.3, 130.8, 129.2, 128.7, 127.3, 124.4, 124.4, 123.8, 104.5, 29.1, 29.1, 24.4, 24.2, 24.1, 21.6. ^{19}F NMR (376 MHz, CD_2Cl_2): δ −76.70. IR (CH_2Cl_2): 1669 cm^{-1} ($\nu_{C=O}$). HRMS (ESI) calcd. (found) for $C_{37}H_{44}AuN_2O_4S$ (M^+): 867.2712 (867.2708).

[(IPr)AuCH(4-picoline)CO$_2$Et]$^+$ OTf$^-$ (2a). 4-Picoline (11.3 μL, 0.116 mmol) was added dropwise to a solution of **1a** (80 mg, 9.7 × 10^{-2} mmol) in CH_2Cl_2 (3 mL) at 25 °C and the resulting solution was stirred for 30 min and then concentrated under vacuum. The resulting residue was crystallized via vapor diffusion of pentane into a concentrated CH_2Cl_2 solution at −20 °C to give **2a** (12 mg, 55%) as white crystals. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.84 (d, *J* = 6.2 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 6.2 Hz, 2H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.32 (s, 2H), 4.96 (s, 1H), 3.96 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.80 (dq, *J* = 10.7, 7.1 Hz, 1H), 2.60 (s, 3H), 2.53 (sept, 6.8 Hz, 1H), 2.51 (sept, 6.8 Hz, 1H), 2.49 (sept, 6.8 Hz, 1H), 2.46 (sept, 6.8 Hz, 1H), 1.27 (d, *J* = 6.8 Hz, 6H), 1.25 (d, *J* = 6.8 Hz, 6H), 1.23 (d, *J* = 6.8 Hz, 6H), 1.15 (d, *J* = 6.8 Hz, 6H), 1.05 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 173.5, 157.7, 146.4, 145.4, 134.3, 131.2, 127.7, 124.8, 124.3, 77.0, 61.3, 29.2, 24.8, 24.1, 22.0, 14.3. HRMS (ESI) calcd. (found) for $C_{37}H_{49}AuN_3O_2$ (M^+): 764.3485 (764.3496).

[(IPr)AuCH(4-picoline)C(O)(4-C$_6$H$_4$Me)]$^+$ OTf$^-$ (2b). 4-Picoline was added dropwise via syringe to a solution of **1b** (27 mg, 3.2 × 10^{-2} mmol) in benzene (2 mL) and stirred at room temperature for 1 h to form a yellow solution. The reaction mixture was cooled at −20 °C to form a precipitate as the benzene froze. The frozen mixture was then warmed to room temperature to form a suspension. The solution phase was decanted from the precipitate, which was rinsed with hexanes and dried under vacuum. The precipitate was then dissolved in diethyl ether containing one drop of CH_2Cl_2 and cooled at −20 °C to form thin crystals. The solution was decanted from the crystals, which were washed with hexanes and dried under vacuum to give **2b** (18 mg, 61%) as thin white crystals. Slow liquid/liquid diffusion of hexanes into a concentrated CH_2Cl_2 solution gave crystals of **2b** suitable for X-ray diffraction. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.87 (d, *J* = 6.3 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 6.3 Hz, 2H), 7.38 (d, *J* = 7.8, 2H), 7.28 (d, *J* = 0.9 Hz, 2H), 7.22 – 7.18 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.10 (s, 1H), 2.62 (s, 3H), 2.45 (sept, 6.8 Hz, 1H), 2.42 (sept, 6.8 Hz, 1H), 2.40 (s, 3H), 2.37 (sept, 6.8 Hz, 1H), 2.33 (sept, 6.8 Hz, 1H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.14 (d, *J* = 6.9 Hz, 6H), 0.81 (d, *J* = 6.9 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 191.7, 185.6, 157.0, 145.9, 145.8, 145.2, 143.2, 133.8, 132.1, 130.6, 129.2, 127.2, 127.0, 124.2, 124.2, 123.7, 84.2, 28.8, 28.6, 24.2, 23.8, 23.7, 23.6, 21.6, 21.3. HRMS (ESI) calcd. (found) for $C_{42}H_{51}AuN_3O$ (M^+): 810.3692 (810.3696).

[(IPr)AuCH(SMe$_2$)CO$_2$Et]$^+$ OTf$^-$ (3a). Dimethyl sulfide (7.6 μL, 1.0 × 10^{-2} mmol) was added via syringe to a solution of **1a** (30 mg, 3.5 x 10^{-2} mmol) in CH_2Cl_2 (3 mL) at room temperature. The resulting solution was stirred for 18 h and then concentrated under vacuum. The resulting white solid was recrystallized from toluene at room temperature to give **3a** (16 mg, 48%) as colorless crystals. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.56 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 1.5 Hz, 2H), 7.34 (d, *J* = 1.5 Hz, 2H), 7.31 (s, 2H), 3.89 (dq, *J* = 10.7, 7.1 Hz, 2H), 3.84 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.41 (s, 1H), 2.51 (sept, *J* = 7.0 Hz, 2H), 2.47 (sept, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.27 (s, 3H), 1.28 (d, *J* = 6.9 Hz, 6H), 1.27 (d, *J* = 6.9 Hz, 6H), 1.24 (d, *J* = 6.9 Hz, 12H), 0.99 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): δ 185.0, 170.6, 145.9, 133.7, 131.0, 124.3, 123.9, 61.1, 49.2, 28.8, 28.8, 28.5, 27.2, 24.4,

24.3, 23.7, 23.7, 13.9. HRMS (ESI) calcd. (found) for $C_{33}H_{48}AuN_2O_2S$ (MH^+): 733.3097 (733.3102).

[(IPr)AuCH(SMe$_2$)C(O)(4-C$_6$H$_4$Me)]$^+$ OTf$^-$ (3b). Dimethyl sulfide (10 μL, 1.4×10^{-2} mmol) was added via syringe to a solution of **1b** (40 mg, 4.6×10^{-2} mmol) in benzene (3 mL) at room temperature. The resulting solution was stirred for 18 h at room temperature and then cooled at –20 °C, forming a precipitate as the benzene froze. The frozen mixture was warmed to room temperature and the thawed benzene solution was decanted from the precipitate, which was rinsed with hexanes and dried under vacuum. The resulting solid residue was dissolved in diethyl ether containing one drop of CH_2Cl_2 and cooled at –20 °C to give **3b** (18 mg, 42%) as a white solid. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.59 (t, *J* = 7.8 Hz, 2H), 7.48 – 7.42 (m, 4H), 7.38 (d, *J* = 7.9 Hz, 4H), 7.28 (s, 2H), 7.15 (d, *J* = 7.8, 2H), 6.96 (d, *J* = 7.8, 2H), 4.80 (s, 1H), 2.52 (s, 3H), 2.50 (sept, 6.9 Hz, 1H), 2.47 (sept, 6.9 Hz, 1H), 2.43 (sept, 6.9 Hz, 1H), 2.39 (sept, 6.9 Hz, 1H), 2.41 (s, 3H), 2.20 (s, 3H) 1.26 (d, *J* = 6.9 Hz, 6H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.16 (d, *J* = 6.9 Hz, 6H), 1.05 (d, *J* = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 193.3, 185.3, 145.7, 145.7, 143.4, 133.6, 132.8, 130.8, 129.1, 128.3, 127.4, 124.1, 124.1, 123.7, 61.6, 31.6, 28.8, 28.7, 28.3, 26.7, 24.3, 24.0, 23.7, 22.7, 21.4, 13.9. HRMS (ESI) calcd. (found) for $C_{38}H_{50}AuN_2OS$ (MH^+): 779.3304 (779.3304).

[(IPr)AuCH(SPh$_2$)CO$_2$Et]$^+$ OTf$^-$ (4a). A solution of (IPr)Au(OTf) (32 mg, 4.3 x 10^{-2} mmol) and Ph_2SCHCO_2Et (35 mg, 0.129 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature for 15 min. The resulting solution was concentrated under vacuum and layered with hexanes at room temperature to give **4a** (37 mg, 85%) as colorless crystals. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.59 – 7.52 (m, 4H), 7.48 (d, *J* = 4.8 Hz, 4H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.31 – 7.27 (m, 6H), 7.25 (s, 2H), 4.36 (s, 1H), 3.81 (dq, *J* = 10.1, 7.3 Hz, 1H), 3.61 (dq, *J* = 10.1, 7.3 Hz, 1H), 2.42 (sept, 4H), 1.19 (t, *J* = 7.8 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 6H), 0.94 (t, *J* = 7.2 Hz, 3H).^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 183.8, 168.7, 145.7, 145.7, 133.5, 133.4, 133.4, 131.5, 131.1, 130.9, 130.8, 129.1, 128.3, 127.6, 124.2, 124.1, 124.0, 61.5, 50.7, 28.7, 24.4, 24.3, 23.6, 23.5, 13.7. HRMS (ESI) calcd. (found) for $C_{43}H_{52}AuN_2O_2S$ (M^+): 857.3410 (857.3417).

[(IPr)AuCH(SPh$_2$)C(O)(4-C$_6$H$_4$Me)]$^+$ OTf$^-$ (4b). A solution of (IPr)Au(OTf) (25 mg, 3.4×10^{-2} mmol) and $Ph_2SCHC(O)(4\text{-}C_6H_4Me)$ (11 mg, 3.4×10^{-2} mmol) in CH_2Cl_2 (2 mL) was stirred at 0 °C for 18 h. The resulting solution was concentrated under vacuum and layered with hexanes at –20 °C to give **4b** (18 mg, 49%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 7.9, 1.9 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.40 – 7.32 (m, 7H), 7.16 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.14 (s, 2H), 7.02 (d, *J* = 8.0, 1.3 Hz, 2H), 7.01 (d, *J* = 8.0, 1.3 Hz, 2H), 6.03 (s, 1H), 2.40 (s, 3H), 2.36 (sept, *J* = 6.9 Hz, 2H), 2.28 (sept, *J* = 6.9 Hz, 2H), 1.23 (d, *J* = 6.9 Hz, 6H), 1.15 (d, *J* = 6.8 Hz, 6H), 1.10 (d, *J* = 6.9 Hz, 6H), 0.91 (d, *J* = 6.9 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 191.5, 184.5, 145.7, 144.4, 133.8, 133.4, 133.3, 131.5, 131.1, 131.0, 130.1, 129.8, 128.7, 128.1, 124.5, 124.4, 124.3, 61.0, 32.0, 29.1, 29.0, 24.8, 24.3, 24.1, 23.9, 23.1, 21.8, 14.3. HRMS (ESI) calcd. (found) for $C_{48}H_{54}AuN_2OS$ (M^+): 903.3617 (903.3622).

[(IPr)AuC(4-picoline)(CO$_2$Me)$_2$]$^+$ OTf$^-$ (5) A solution of 4-picolinium bis(carbomethoxy)methylide (15 mg, 6.9×10^{-2} mmol and (IPr)Au(OTf) (25 mg, 6.2×10^{-2} mmol) in CH_2Cl_2 (2 mL) was stirred at 25 °C for 18 h. The resulting solution was concentrated under vacuum and layered with hexanes to give **5** (51 mg, 70%) as off-white crystals. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 6.4 Hz, 2H), 7.65 (t, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 6.3 Hz, 2H), 7.43 (s, 2H), 7.39 (d, *J* = 7.8 Hz, 4H), 3.41 (s, 6H), 2.66 (s, 3H), 2.47 (sept, *J* = 6.9 Hz, 4H), 1.25 (d, *J* = 6.8 Hz, 12H) 1.22 (d, *J* = 6.8 Hz, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 181.0, 167.7, 161.1, 148.0, 146.0, 133.6, 131.3, 127.7, 124.5, 124.3, 91.0, 52.7, 28.9, 24.5, 24.1, 22.2.

[(IPr)AuC(SPh$_2$)(CO$_2$Me)$_2$]$^+$ OTf$^-$ (6). A solution of diphenylsulfoxonium bis(carbomethoxy)methylide (22 mg, 6.9×10^{-2} mmol) in CH_2Cl_2 (1 mL) was added dropwise to a solution of (IPr)Au(OTf) (46 mg, 6.2×10^{-2} mmol) in CH_2Cl_2 (1 mL) and stirred at 25 °C for 18 h. The resulting solution was concentrated under vacuum and layered with hexanes to give **6** (22 mg, 39%) as off-white crystals. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.61 (t, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 6.8 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 4H), 7.38 – 7.33 (m, 8H), 7.31 (s, 2H), 3.38 (s, 3H), 3.37 (s, 3H), 2.47 (sept, *J* = 7.0 Hz, 4H), 1.23 (d, *J* = 6.9 Hz, 12H), 1.19 (d, *J* = 6.8 Hz, 12H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 180.0, 166.6, 146.2, 134.0, 133.7, 131.5, 131.4, 130.8, 127.4, 124.8, 124.7, 71.0, 54.3, 54.1, 53.8, 53.6, 53.5, 53.4, 29.2, 24.5, 24.0.

7. A suspension of **1b** (15 mg, 1.7×10^{-2} mmol) in cyclohexene (1 mL) was heated at 75 °C for 18 h. As the mixture heated, **1b** dissolved, followed by the slow precipitation of IPrAuOTf as the reaction progressed. The resulting mixture was filtered through a plug of silica gel and concentrated under vacuum. ^{1}H NMR analysis of the oily residue established the formation of **7** in 33% yield as determined by integrating the aromatic resonance of **7** at δ 7.87 relative to the resonance of CH_2Br_2 internal standard. The structure and exo configuration of **7** was established by comparison to an authentic sample synthesized employing the method of Takebayashi.[44,45] To this end, a solution of *p*-methyl-2-diazoacetophenone (250 mg, 1.6 mmol) and $Cu(acac)_2$ (5 mg, 1.9×10^{-2} mmol) in cyclohexene (8 mL) was heated at 75 °C for 30 min. The reaction mixture was cooled to room temperature, filtered through a plug of silica gel, and concentrated under vacuum. The resulting brown residue was chromatographed (SiO_2; hexanes-EtOAc = 9:1) to give *cis*-**7** (104 mg, 31%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 2H), 2.47 (t, *J* = 4.2 Hz, 1H), 2.43 (s, 3H), 2.05 – 1.96 (m, 2H), 1.92 – 1.90 (m, 2H), 1.82 – 1.77 (m, 2H), 1.46 – 1.25 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 199.81, 143.1, 135.9, 129.1, 128.0, 31.3, 26.4, 23.3, 21.6, 21.2. HRMS (ESI) calcd (found for $C_{15}H_{19}O$ (MH^+): 215.1436 (215.1434).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information material is available free of charge via the Internet at http://pubs.acs.org.
Scans of NMR spectra.

Accession Codes

CCDC 1976627 – 1976630 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 interests.

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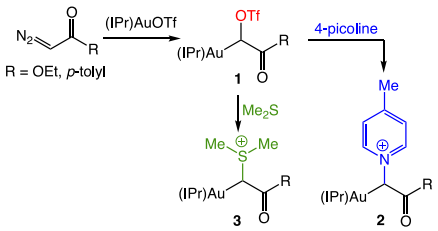
N2
O
R
R = OEt, p-tolyl
(IPr)AuOTf
OTf
(IPr)Au
R
1
O
4-picoline
Me
Me2S
Me
S
Me
(IPr)Au
R
3
O
N
(IPr)Au
R
2
O