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Synthesis and Reactivity of Air-Stable N-Heterocyclic Carbene Gold(I) Bis(trifluoromethanesulfonyl)imidate Complexes

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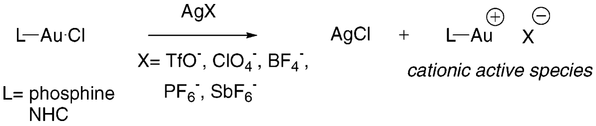
Summary: A study concerning the synthesis of new N-heterocyclic carbene gold(I) complexes using the bis(trifluoromethanesulfonyl)imidate moiety (Tf_2N^-*) as a weakly coordinating counteranion is described. These new air-stable (NCH)AuNTf*$_2$ *complexes are convenient to prepare, stoe, and handle and proved to be active in a range of gold(I)-catalyzed transformations.*

Gold(I) complexes have recently emerged as efficient and mild catalysts for the activation of alkynes or allenes toward addition by a variety of nucleophiles.[1] However, despite its efficiency, the catalytic system generally employed in these transformations,[2] which corresponds to the combined use of a phosphine or N-heterocyclic carbene gold(I) chloride complex and a silver salt as a cocatalyst (Scheme 1), suffers from some limitations. The silver salts are all very hygroscopic, causing difficulties in the proper weighing of the reagent and in keeping the reaction medium nonacidic.[3] Moreover, the cationic active gold(I) species is quite unstable, especially when a fluorine-based counteranion is used,[4] and may therefore not be isolable in most of the cases.[5]

Scheme 1. General Formation of Active Gold(I) Species



As part of our work on gold(I) catalysis, we recently reported that a variety of phosphine gold(I) complexes bearing the bis(trifluoromethanesulfonyl)imidate moiety (Tf_2N^-) as a weakly coordinating counteranion could be easily synthesized by a metathesis reaction between the corresponding gold(I) phosphine chloride complexes and silver(I) bis(trifluoromethanesulfonyl)imidate ($AgNTf_2$).[6] These complexes were isolated as crystalline compounds and proved to be stable toward air and moisture. Moreover, their evaluation in various catalytic transformations initially revealed that they were, most of the time, at least as active as other catalytic systems. Following these preliminary results, several reports by ourselves[7] and others[8] have emphasized the interest of these very convenient complexes in the development of numerous gold(I)-catalyzed transformations.

While phosphines are most commonly used as ligands to stabilize the gold(I) center, recent publications have shown that the use of strongly σ-donating N-heterocyclic carbene (NHC) ligands could be beneficial in cases where the use of phosphine led to a poor or moderate catalytic activity of the gold(I) complexes.[9] Interestingly, Nolan and co-workers have recently reported the synthesis of complex **1** in a study dedicated to the synthesis and the isolation of stable yet reactive NHC−gold(I) complexes (Scheme 2).[10] Even though this cationic species was the most stable complex observed so far, the synthetic route employed could not be generalized to the formation and isolation

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(1) For recent reviews on gold catalysis, see: (a) Gorin, D. J.; Toste, F. D. *Nature* **2007**, *46*, 395−403. (b) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 2−42. (c) Hashmi, S. A.; Huchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896−7936. For selected recent examples of gold(I)-catalyzed reactions, see: (d) Lee, J. H.; Toste, F. D. *Angew. Chem., Int. Ed.* **2007**, *46*, 912−914. (e) Witham, C. A.; Mauleon, P.; Shapiro, N. D.; Sherry, B. D.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 5838−5839. (f) Hashmi, S. A.; Salathé, R.; Frey, W. *Eur. J. Org. Chem.* **2007**, 1648−1652. (g) Zhang, Z.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2007**, *45*, 283−285. (h) Binder, J. T.; Crone, B.; Kirsch, S. F.; Liébert, C.; Menz, H. *Eur. J. Org. Chem.* **2007**, 1636−1647. (i) Huang, X.; Zhang, L. *J. Am. Chem. Soc.* **2007**, *129*, 6398−6399. (j) López, S.; Herrero-Gómez, E.; Pérez-Galán, P.; Nieto-Oberhuber, C.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2006**, *44*, 6029−6032. (k) Sun, J.; Conley, M. P.; Zhang, L.; Kozmin, S. A. *J. Am. Chem. Soc.* **2006**, *128*, 9705−9710.

(2) Protonation of an alkylgold(I) complex with a strong acid may also be used to generate the cationic species; however, these conditions are not always compatible with the substrates.

(3) The use of a glovebox is required to properly weigh the silver salt.

(4) Weakly coordinating anions such as BF_4^-, PF_6^-, and SbF_6^- are Lewis acid/base conjugates of a superior nucleophile (e.g., $MF_{n+1}^- \rightarrow MF_n + F^-$). Their ability to act as inert counterions is always limited by a competition reaction for that nucleophile (e.g., F^-), and the free Lewis acid MF_n can act as an oxidizing agent and thus cause unwanted side reactions. See: (a) Raabe, I.; Krossing, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 2066−2090. (b) Raabe, I.; Krossing, I. *Chem. Eur. J.* **2004**, *10*, 5017−5030.

(5) Echavarren and co-workers have reported the isolation of the two air-stable cationic complexes $(Ph_3P)Au(NCMe)SbF_6$ and (2-(di-*tert*-butylphosphino)biphenyl)Au(NCMe)SbF$_6$ as active catalysts for cycloisomerization. See: (a) Nieto-Oberhuber, C.; López, S.; Munoz, M. P.; Cardenas, D. J.; Bunuel, E.; Nevado, C.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6146−6148. (b) Ferrer, C.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1105−1109. (c) Nieto-Oberhuber, C.; Munoz, M. P.; López, S.; Jimenez-Nunez, E.; Nevado, C.; Herrero-Gomez, E.; Raducan, M.; Echavarren, A. M. *Chem. Eur. J.* **2006**, *12*, 1677−1693.

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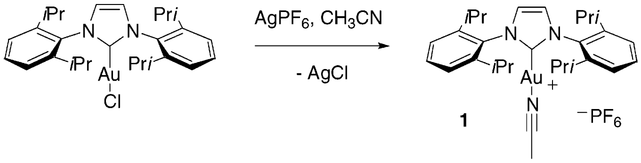
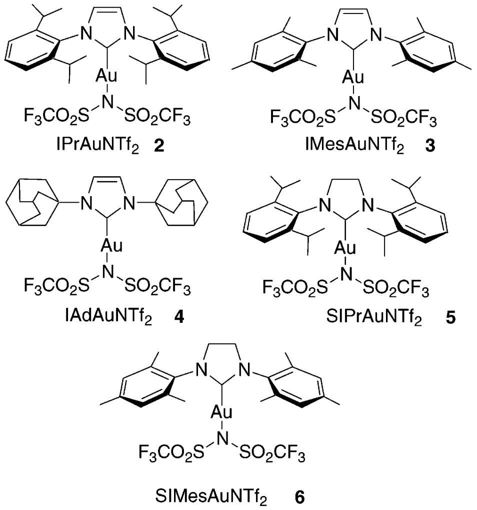
10.1021/om7006002 CCC: $37.00

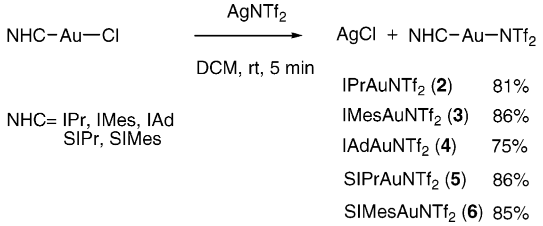
Scheme 2. Synthesis of $IPrAu(NCMe)PF_6$ (1) by Nolan and Co-Workers



Scheme 3. NHC Gold(I) Complexes Envisaged



Scheme 4. Synthetic Route to $(NHC)AuNTf_2$ Complexes



of other stable NHC−gold(I) complexes. Moreover, complex **1** was unstable in solution and slow decomposition took place in acetonitrile within a few days, leading to the observance of colloidal gold(0).

By analogy with our previously reported work,[6] we surmised that the bis(trifluoromethanesulfonyl)imidate moiety could be used as a weakly coordinating counteranion for the synthesis of stable and catalytically active NHC−gold(I) complexes. To this end, we focused our attention on the synthesis of gold(I) complexes **2**−**6**, bearing the most commonly used IPr, IMes, IAd, SIPr, and SIMes NHC ligands (Scheme 3).[11]

The previously reported IPrAuCl, IMesAuCl, IAdAuCl, SIPrAuCl, and SIMesAuCl complexes[12] were dissolved in dichloromethane, and 1 equiv of silver bis(trifluoromethanesulfonyl)imidate ($AgNTf_2$) was added (Scheme 4). This led to the rapid precipitation of silver chloride, which was removed by filtration through Celite after stirring for 5 min.

The novel complexes **2**, **4**, and **5**, possessing respectively the IPr, IAd, and SIPr NHC ligands, were fully stable in solution even after a prolonged time (1 day), while the appearance of colloidal gold(0) could be observed after 3 h in the case of $SIMesAuNTf_2$ (**6**) and after 10 h in the case of $IMesAuNTf_2$ (**3**). Complexes **2**, **4**, and **5** could be isolated as white products after simple evaporation of the solvent, while complexes **3** and **6** led to the isolation of a greyish powder, as the result of a partial decomposition of the material. All these complexes could, however, be obtained as stable white powders by evaporation of the major part of the dichloromethane followed by precipitation of the complexes with pentane. By this procedure, the $(NHC)AuNTf_2$ complexes **2**−**6** were obtained in yields ranging from 75% to 86%.[13] It is noteworthy that all of these complexes were stable in the solid state, with the exception of the SIMes derivative **6**, which turned gray within a few days. Complexes **2**−**6** were fully characterized by ^{1}H NMR and ^{13}C NMR spectroscopic analysis (Table 1).[13] The ^{1}H NMR spectra of complexes **2**−**4**, containing unsaturated NHC ligands, are characterized by a single resonance at low field for the two imidazole ring protons (7.24−7.33 ppm), while the resonances of the imidazoline ring protons in the saturated complexes **5** and **6** occur respectively at 4.20 and 4.14 ppm. All of these NHC protons appear to be shifted slightly downfield (0.09−0.19 ppm) compared to those in the corresponding (NHC)AuCl precursors. It is also interesting to note that complex **1** exhibits the greatest downfield shift of the imidazole ring protons in the IPr series. This might be interpreted as a lower electron density in the imidazolium ring resulting from a better σ donation of the IPr ligand to a gold center presenting a more pronounced cationic character. It may therefore be assumed that $IPrAu(NCMe)PF_6$ (**1**) is a more powerfully electrophilic species than the newly synthesized $IPrAuNTf_2$ (**2**). The carbene carbons in these new complexes appear closer to the corresponding (NHC)AuCl resonance, but slightly upfield (5−9.1 ppm). They resonate between 157.2 and 168.3 ppm for unsaturated complexes **2**−**4** and at 190.0 and 190.4 ppm for the saturated complexes **5** and **6**.

Table 1. Comparative ^{1}H NMR and ^{13}C NMR Data for (NHC)AuCl, $(NCH)AuNTf_2$, and $IPrAu(NCMe)PF_6$ (1) Complexes

complex	solvent	δ_H(NHC)[a]	δ_C(Au−C)
IPrAuCl[b]	CD_2Cl_2	7.24	175.0
$IPrAuNTf_2$ (**2**)	CD_2Cl_2	7.33	167.6
$IPrAu(NCMe)PF_6$ (**1**)[c]	CD_3CN	7.66	168.3
IMesAuCl[b]	$CDCl_3$	7.09	173.4
$IMesAuNTf_2$ (**3**)	CD_2Cl_2	7.28	166.7
IAdAuCl[b]	CD_2Cl_2	7.08	166.3
$IAdNTf_2$ (**4**)	CD_2Cl_2	7.24	157.2
SIPrAuCl[b]	$CDCl_3$	4.06	196.1
$SIPrAuNTf_2$ (**5**)	CD_2Cl_2	4.20	190.4
SIMesAuCl[b]	$CDCl_3$	3.98	195.0
$SIMesAuNTf_2$ (**6**)	CD_2Cl_2	4.14	190.0

[a] Resonance of the corresponding imidazole or imidazoline ring protons. [b] Reference 11. [c] Reference 9.

X-ray diffraction was finally used to unambiguously determine the structure of these new complexes. X-ray-quality crystals were grown in a mixture of dichloromethane and pentane for complexes **2**−**4**.[13] Despite all our efforts, we were not able to obtain crystals suitable for X-ray analysis in the case of the saturated complexes **5** and **6**. Ball-and-stick representations are shown in Figures 1−3.

All new complexes have a two-coordinated gold(I) atom, in a nearly linear arrangement with C(1)−Au−N(3) bond angles close to 180° (from 177.4 to 178.0°). For all X-ray-characterized complexes, the Au−C(1) bond distances range from 1.969 to 1.985 Å. These distances are in agreement with those previously

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(11) During the preparation of this paper, Zhang and co-workers reported the use of the $IPrAuNTf_2$ complex in the gold-catalyzed intramolecular redox reaction of sulfinylalkynes: Li, G.; Zhang, L. *Angew. Chem., Int. Ed.* **2007**, *46*, 5156−5159. However, the authors did not give information about the synthesis and isolation of this complex.

(12) De Frémont, P.; Scott, N. M.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 2411−2418.

(13) See the Supporting Information.

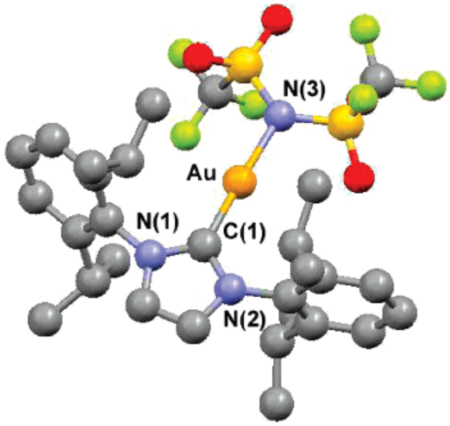


Figure 1. Molecular structure of IPrAuNTf$_2$ (**2**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Au−C(1) = 1.969(2), Au−N(3) = 2.091(2); C(1)−Au−N(3) = 178.0(1).

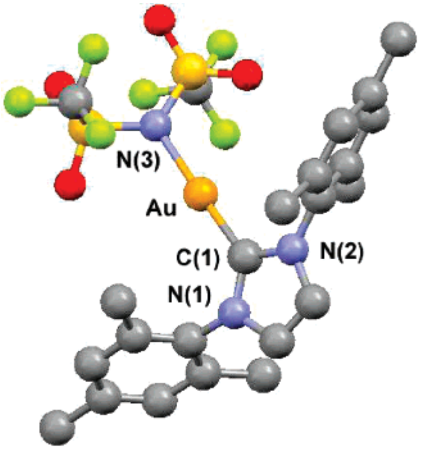


Figure 2. Molecular structure of IMesAuNTf$_2$ (**3**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Au−C(1) = 1.976(3), Au−N(3) = 2.077(2); C(1)−Au−N(3) = 177.4(1).

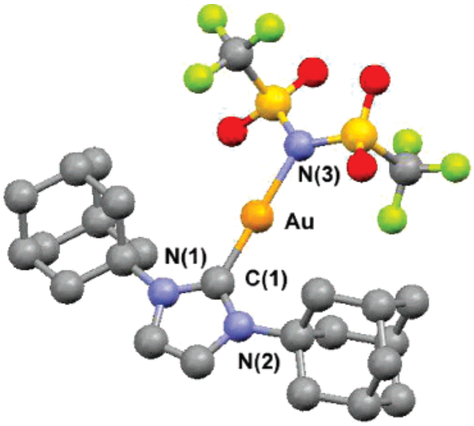
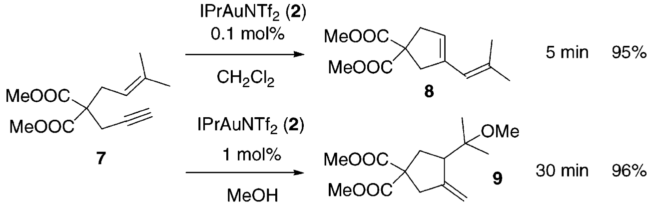


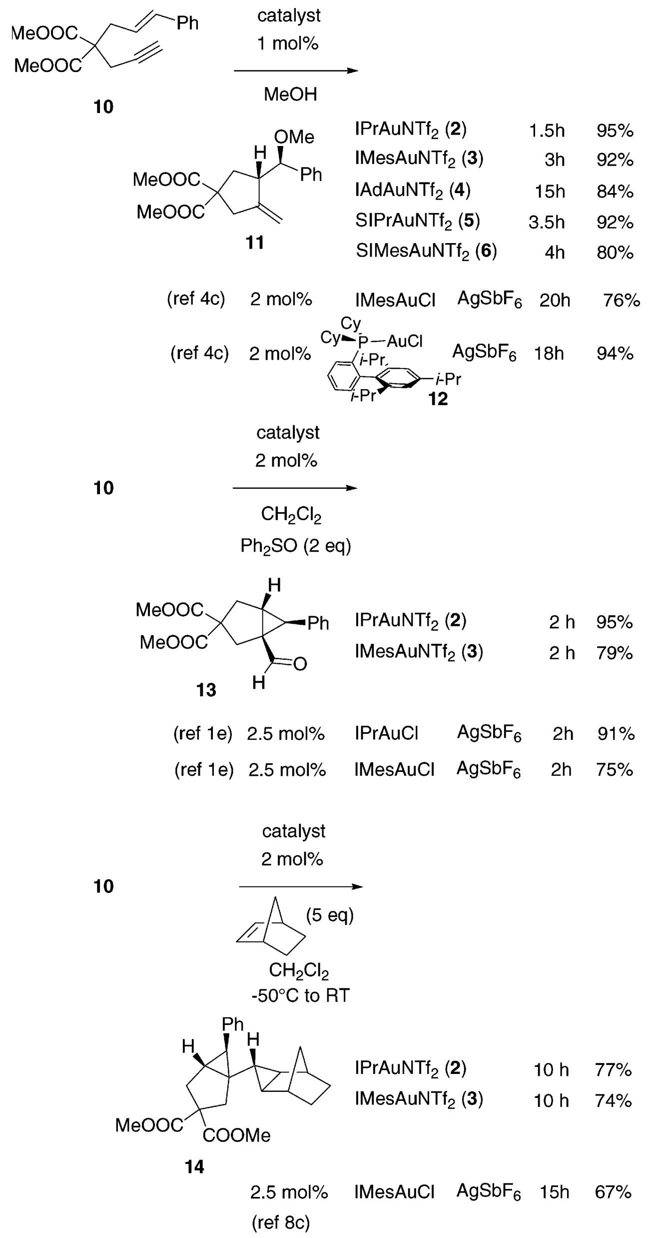
Figure 3. Molecular structure of IAdsAuNTf$_2$ (**4**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Au−C(1) = 1.985(3), Au−N(3) = 2.094(2), C(1)−Au−N(3) = 177.6(1).

reported for other (NHC)Au^I complexes and are slightly shorter than those observed in the corresponding (NHC)AuCl precursors.[12] The Au−N(3) bond distances, which lie in the range 2.077−2.094 Å, are slightly longer than that observed in the case of the cationic complex IPrAu(NCMe)PF$_6$ (**1**) (2.022 Å).[10]

Scheme 5. IPrAuNTf$_2$-Catalyzed Cycloisomerization and Methoxycyclization of Enyne 7



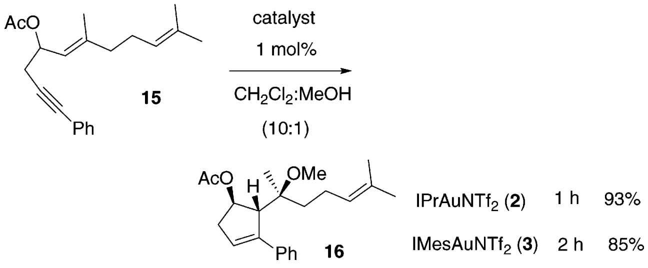
Scheme 6. (NHC)AuNTf$_2$-Catalyzed Transformations of Enyne 10



These new air-stable gold(I) complexes (**2**−**6**), which were easily synthesized and isolated, were then tested in a range of previously reported gold(I)-catalyzed transformations. The simple enyne **7** was first chosen as a model substrate (Scheme 5).

When the reaction was performed in dichloromethane with only 0.1 mol % of **2** as the catalyst, we were delighted to observe the rapid formation of metathesis product **8**, which was isolated in an excellent 95% yield.[5c,6] Changing the solvent to methanol and increasing the loading of the catalyst to 1 mol % led to the

Scheme 7. (NHC)AuNTf$_2$-Catalyzed 5-Endo Methoxycyclization of Enyne 15



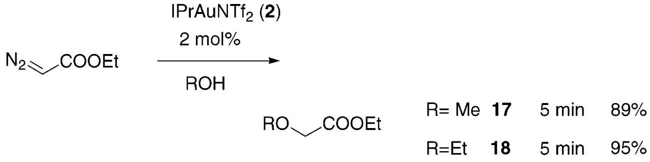
rapid and clean formation of the methoxylated product **9**. It has to be noted that this latter result is among the best reported to date.[5c,6]

We next turned our attention to a series of gold(I)-catalyzed transformations of enyne **10** (Scheme 6). Methoxycyclization of enyne **10** into **11** was reported by Echavarren and co-workers to need reaction times longer than those required to cyclize **7** into **9**.[5c] The best result was obtained in their case by using 2 mol % of the biphenylphosphine-based catalyst **12**. Completion was observed after 18 h and product **11** isolated in 94% yield. We were highly surprised to see that the same transformation was much more rapid when the (NHC)AuNTf$_2$ complexes were used as the catalysts. Using only 1 mol % of the catalysts, completion was generally obtained in less than 4 h (with the exception of complex **4**) and the product isolated in high yield. It is interesting to note that a simple change in the nature of the counteranion (SbF_6^- for Tf_2N^-) led to a much faster conversion of enyne **10** into **11** when catalyst **3** was used instead of the (IMesAuCl + AgSbF$_6$) catalytic system. Complexes **2** and **3** also efficiently catalyzed the oxidative cyclization of enyne **10** into aldehyde **13**[1e] and the formation of polycyclic compound **14**,[9c] as previously reported by the groups of Toste and Echavarren. The results obtained with complexes **2** and **3** were comparable to those obtained when using the ((NHC)AuCl + AgSbF$_6$) catalytic system.

The same catalysts were also succesfully employed in the stereospecific 5-endo methoxycyclization of enyne **15** (Scheme 7).[7b] The use of 1 mol % of IPrAuNTf$_2$ led to the clean formation of cyclopentene **16**, which was isolated after 1 h of reaction in 93% yield. The transformation was slower, however, in the case of the less stable IMesAuNTf$_2$ complex, which led to the isolation of **16** in a slightly diminished 85% yield.

We finally tested the activity of IPrAuNTf$_2$ in the gold(I)-catalyzed carbene-transfer reaction recently described by Nolan and co-workers.[9d,10] The reaction of ethyl diazoacetate with methanol or ethanol in the presence of 2 mol % of the IPrAuNTf$_2$ complex **2** led to the rapid formation of the corresponding methyl and ethyl ethers **17** and **18**, respectively, in 89% and 95% yield (Scheme 8). However, while the IPrAu(NCMe)PF$_6$ complex **1** was described to be a relatively efficient catalyst for the insertion of the :CHCOOEt unit into the N−H bond of aniline and *tert*-butylamine, the IPrAuNTf$_2$ complex **2** was completely inert to this transformation.

Scheme 8. IPrAuNTf$_2$-Catalyzed Carbene Transfer Reaction



In summary, we have developed a new class of NHC−gold(I) complexes based on the use of the bis(trifluoromethanesulfonyl)imidate moiety as a weakly coordinating counteranion. Five complexes have been isolated and characterized by NMR spectroscopy, and three of them have been characterized by X-ray analysis. The air-stable IPrAuNTf$_2$ (**2**), IMesAuNTf$_2$ (**3**), IAdAuNTf$_2$ (**4**), and SIPrAuNTf$_2$ (**5**) are convenient to prepare, store, and handle. These gold(I) complexes have been tested as catalysts in a range of reactions and proved to be, in most of the cases, at least as active as other catalytic systems generally employed for such transformations. Further studies relating to the use of these new (NHC)AuNTf$_2$ complexes in catalyzed synthetic transformations, as well as studies aimed at developing new active, air-stable gold catalysts are currently underway.

Acknowledgment. We wish to thank Prof. S. Z. Zard for helpful discussions and Rhodia Chimie Fine for a gift of HNTf$_2$.

Supporting Information Available: Text, figures, and tables giving synthetic details for **2**−**6** and details of the catalysis experiments and CIF files giving crystallographic data for complexes **2**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org. These files have also been deposited with the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K., and can be obtained on request free of charge, by quoting the publication citation and deposition numbers 650547−650549.

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