Carbenoids

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Gold(I) Carbenoids: On-Demand Access to Gold(I) Carbenes in Solution

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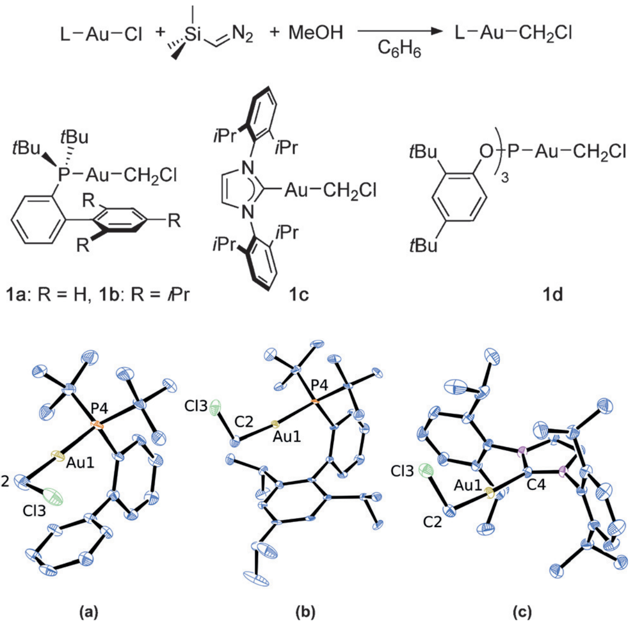
In memory of José Barluenga

Abstract: *Chloromethylgold(I) complexes of phosphine, phosphite, and N-heterocyclic carbene ligands are easily synthesized by reaction of trimethylsilyldiazomethane with the corresponding gold chloride precursors. Activation of these gold(I) carbenoids with a variety of chloride scavengers promotes reactivity typical of metallocarbenes in solution, namely homocoupling to ethylene, olefin cyclopropanation, and Buchner ring expansion of benzene.*

Carbene complexes of transition metals are reactive intermediates[1] frequently invoked in a wide variety of C–C bond-forming processes that range from industrial scale olefin metathesis[2] to natural product synthesis.[3] Despite their central role in gold catalysis,[4] few non-heteroatom-stabilized gold(I) carbene complexes have been structurally characterized.[5] The reduced steric shielding provided by commonly used ligands and the intrinsically high electrophilicity[6] exhibited by simple gold(I) carbenes preclude their isolation in condensed phase. Such species are however of high interest as demonstrated by gas-phase studies by Chen,[7] Schwarz,[8] and others.[9] The isolation of this type of compounds, or their functional equivalents, is therefore of great importance for the fundamental understanding of the reactivity of electrophilic gold carbenes. Transition-metal complexes of the type [M(CHXR)], formally defined as carbenoids,[10] show similar reactivity to their carbene counterparts[11] and offer an attractive alternative to otherwise non-isolable species. To date, however, very little is known about gold(I) carbenoids and their reactivity.[12] Herein we report the synthesis of easily accessible gold carbenoids bearing bulky ligands as gold carbene equivalents in solution.

Previous synthesis of chloromethylgold(I) complexes used either toxic and potentially explosive diazomethane[12a] or low-temperature in situ formation of $Mg(CH_2Cl)Cl$.[12d] We have developed a more convenient approach that utilizes the methanol promoted decomposition of trimethylsilyldiazomethane[13,14] at room temperature (Scheme 1). Treatment of phosphine, phosphite, and NHC gold chloride complexes with trimethylsilyldiazomethane in benzene solution in presence of methanol afforded gold carbenoids **1a**–**d** within minutes. Complexes **1a**–**c** could be easily purified by column chromatography and have been fully characterized. Remarkably, these gold(I) carbenoids can be stored indefinitely when protected from air, and only decompose slowly when left under ambient conditions.

Measured Au–C distances (Table 1) are close to 2.088(9) Å observed for the previously reported $[(PPh_3)AuCH_2Cl]$ complex (**2**).[12d] On the other hand, C–Cl distances (1.828–1.830 Å) are markedly longer than found in **2** (1.68(1) Å), and



Scheme 1. Synthesis of chloromethylgold(I) complexes **1a**–**d** and structures of complexes a) **1a**, b) **1b**, c) and **1c**.[38] ORTEP plots with ellipsoids set at 50% probability; hydrogen atoms and solvent molecules are omitted for clarity.

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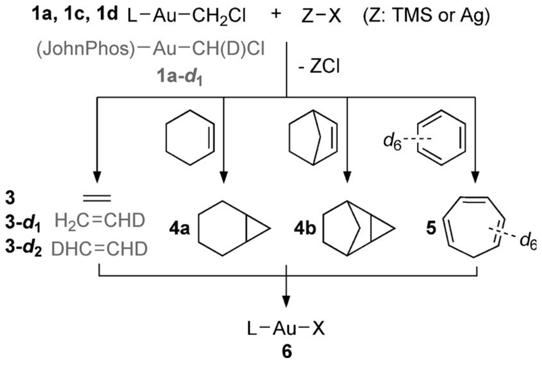
Table 1: Selected bond distances [Å] and angles [°] from solid-state molecular structures and chemical shifts[a] [δ, ppm] for the new carbenoid complexes.

Complex	Au1–C2	C2–Cl3	Au1-C2-Cl3	δ ^{1}H[a]	δ ^{13}C[a]
1a	2.058(9)	1.828(1)	110.3(5)	2.96	53.6
1b	2.088(5)	1.829(5)	111.1(3)	2.94	53.9
1c	2.060(2)	1.830(2)	110.4(1)	3.34	47.2
1d	–	–	–	3.63	49.1

[a] Chemical shifts corresponding to the chloromethyl moiety measured in CD_2Cl_2 solution at 23 °C.

in fact are the longest among all 79 published crystal structures containing a [MCH_2Cl] motif.[15] The longest previously reported C–Cl distance in a (chloromethyl)metal fragment was 1.826(2) Å in a Rh^{III} complex.[16] On the other hand, the Au1-C2-Cl3 angles are closer to the ideal tetrahedron as opposed to the majority of other structures in which the M-C-Cl angle is about 116°.[17] Chemical shifts for the chloromethyl moiety are found between 2.94 and 3.63 ppm in ^{1}H NMR and 47.2 and 53.9 ppm in ^{13}C NMR spectra.

When solutions of complexes **1a–d** were treated with chloride scavengers possessing weakly coordinating counterions, for example, TMSX and AgX ($X = Tf_2N^-$, TfO^-, $MeSO_3^-$, $CF_3CO_2^-$) as well as $AgSbF_6$, formation of ethylene (**3**) and simple gold salts **6** was observed (Scheme 2). Analysis of the volatile products by GC-MS confirmed the identity of ethylene and excluded the formation of any additional organic compounds (Supporting Information, Figure S5). The ^{1}H NMR spectrum obtained upon chloride abstraction on the partially monodeuterated carbenoid **1a-*d*$_1$** (Supporting Information, Figure S1) exhibits signals with characteristic deuterium couplings arising from the formation of the mono- and bi-deuterated ethylenes **3-*d*$_1$**[18] and **3-*d*$_2$**[19] alongside **3**, as expected from the bimolecular ethylene formation. Furthermore, intermediates of the type **7**, in which the chloride has been replaced by the counterion of the scavenger, could be detected in all cases except when using $AgSbF_6$ (Figure 1). The chemical shift for the methylidene resonance of **7a–d** strongly depends on the counterion used and ranged from 3.45 to 5.01 ppm. Despite the apparently counterintuitive trend (chemical shift does not follow the acidity of the counterion), a similar behavior has been observed on the methyl compounds MeX.[20]



Scheme 2. General reactivity of gold carbenoids after activation by chloride scavengers.

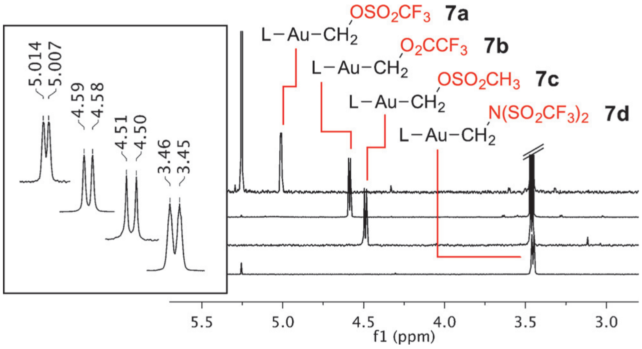
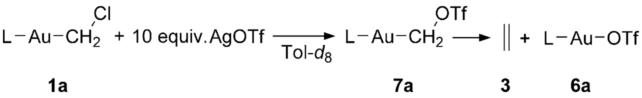


Figure 1. ^{1}H NMR spectra of intermediates **7a–d** obtained by reaction of **1a** with different TMSX reagents in [D_8]toluene solution.

The reaction of **1a** with an excess of AgOTf (Scheme 3) could be conveniently monitored by ^{1}H NMR spectroscopy to obtain accurate kinetic concentration profiles (Supporting Information, Figure S15) of carbenoid **1a**, triflate substituted species **7a**, and the final gold salt **6a**. Even though ethylene was detected by ^{1}H NMR, its signal cannot be accurately integrated owing to its rapid equilibration with the gas phase. For this reason, ethylene was quantified by means of pressure measurements in a closed system (Supporting Information, Figures S3 and S4).



Scheme 3. Reaction of **1a** with excess AgOTf used for the determination of the corresponding activation parameters by ^{1}H NMR spectroscopy.

The consumption of carbenoid **1a** follows a first-order decay as expected from the pseudo first-order conditions employed. Surprisingly, the subsequent decay of intermediate **7a** into complex **6a** and ethylene also follows a first-order kinetic regime contrary to what would be expected for a dimerization process and the reported second order homocoupling of well-characterized methylidene complexes of Ta[21] and Re.[22] A final yield of 60 % ethylene could be quantified independently in the closed system. More importantly, at room temperature the pressure increase, that is, the formation of ethylene, also follows a first-order regime in good agreement with the decay of **7a** observed by NMR. Variable-temperature measurements allowed the determination of the activation parameters for both processes. The initial substitution of chloride for triflate (**1a** to **7a**) exhibits values of $\Delta H^{\ddagger} = 12.9 \pm 0.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -19.2 \pm 2$ cal K^{-1} mol^{-1}, whereas the conversion of **7a** to **3** and ethylene shows values of $\Delta H^{\ddagger} = 15.0 \pm 0.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -21.5 \pm 2$ cal K^{-1} mol^{-1}.

Activation of **1a** in THF suppressed the formation of ethylene and yielded instead a gold-stabilized oxonium ylide **8**

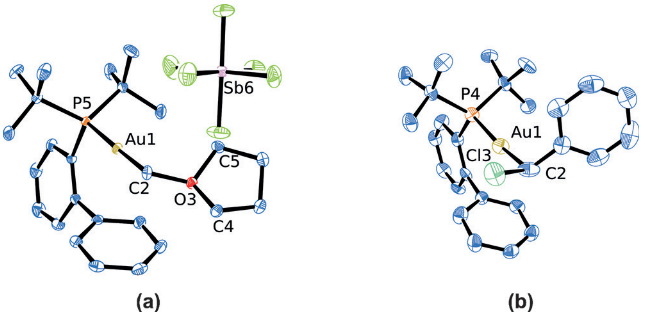


Figure 2. Molecular structures of complexes a) **8** and b) **9**.[38] ORTEP plots with ellipsoids set at 50% probability; solvent molecules and hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°] for **8**: Au1–C2 2.065(2), C2–O3 1.517(2), C4–O3 1.479(2), C5–O3 1.486(2), Au1–P5 2.3069(5); C2-O3-C4 117.8(1), C2-O3-C5 115.4 (1), C4-O3-C5 108.8(1); and **9**: Au1–C2 2.056(1), C2–Cl3 1.838(1), Au1–P4 2.287(2); Au1-C2-Cl3 106.7(5).

(Figure 2). Trapping is irreversible and no ethylene is formed even upon heating of the sample. Despite the lack of reactivity of **8**, its formation hinted at the possibility of an intermolecular trapping of the methylene moiety with a suitable substrate. When the activation of the new carbenoid complexes was carried out in the presence of olefins, methylene transfer to form cyclopropanes **4** alongside ethylene was observed (Scheme 2). This process closely resembles the gold-catalyzed cyclopropanation of olefins with diazo compounds.[23] Thus, complexes **1a** and **1c** could methylenate cyclohexene and norbornene, yielding norcarene **4a** and *exo*-tricyclo[3.2.1.0^{2,4}]octane **4b** in moderate to good yields when activated with either a silver salt or a TMS reagent (Table 2, entries 1a,b–4a,b). Phosphite complex **1d** could only generate traces of cyclopropanes with cyclohexene (Table 2, entries 5a,b and 6a,b). These results highlight the aptitude of good σ-donor and poor π-acceptor ligands (phosphines and *N*-heterocyclic carbenes) to enhance the stabilization of carbene fragments by gold.[4] Cycloheptatriene **5** was formed when the activation of carbenoids **1a** and **1c** was performed in benzene[23a] (Table 2, entries 1c–4c). In this case, initial methylenation to form norcaradiene is followed by electrocyclic opening to yield **5**.[24] Carbenoid **1d** yielded only traces of **5** in parallel with its low reactivity towards cyclopropanation (Table 2, entries 5c, 6c).

Table 2: Yields[a] for methylene transfer from complexes **1a,c,d** to olefins[b] to form cyclopropanes **4a,b** and to benzene[c] to form cycloheptatriene **5** (see Scheme 2).

Entry	Complex	Chloride scavenger	a) **4a**	b) **4b**	c) **5**
1	**1a**	$TMSNTf_2$	51	97	12
2	**1a**	$AgNTf_2$	60	74	7
3	**1c**	$TMSNTf_2$	67	75	28
4	**1c**	$AgNTf_2$	45	51	12
5	**1d**	$TMSNTf_2$	0	0	2
6	**1d**	$AgNTf_2$	4	0	1

[a] Yield determined from ^{1}H NMR spectroscopy (average of two runs). [b] Reactions performed with 0.017 mmol of carbenoid complexes and 20 equiv of olefin in CD_2Cl_2 solution. [c] Same scale as cyclopropanation reactions using [D$_6$]benzene as solvent and substrate.

The formation of gold carbenoids is not limited to the insertion of diazomethane. Reaction of phenyldiazomethane with [(JohnPhos)AuCl] provided chloro(phenyl)methylgold carbenoid **9** (Figure 3). In comparison with its chloromethyl analogues, complex **9** exhibits a longer C–Cl bond at 1.838(1) Å and a more acute Au-C-Cl angle of 106.7(5) degrees.[25] Activation of carbenoid complex **9** with TMSOTf in CD_2Cl_2 solution showed complete consumption of **9** and formation of homocoupling products *cis*- and *trans*-stilbene **10** together with their cyclopropanation product 1,2,3-triphenylcyclopropane **11** among other not identified products (Scheme 4). The observed reactivity closely resembles that previously reported for the transition-metal-catalyzed decomposition of phenyldiazomethane[26] and the cyclopropanation of stilbenes by

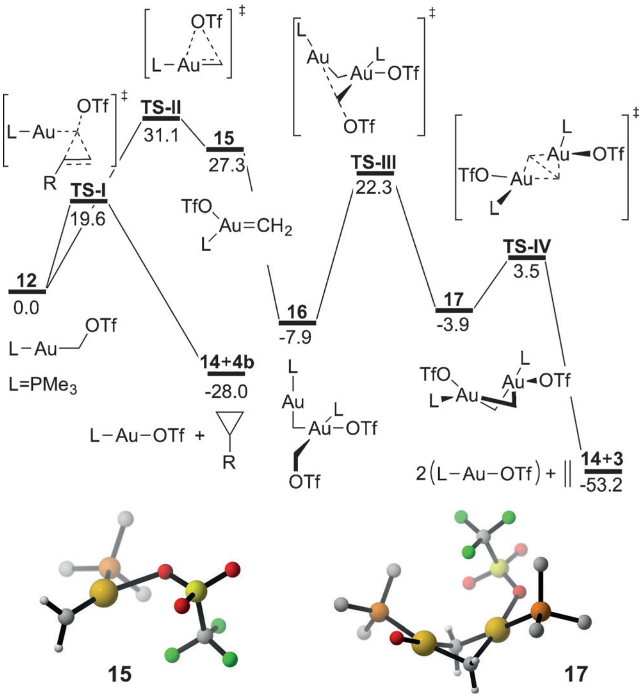
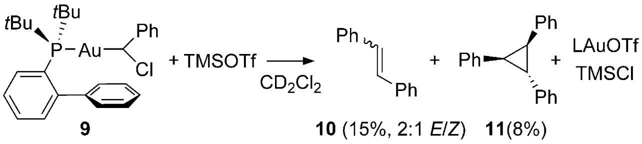


Figure 3. Calculated reaction profiles for the cyclopropanation of norbornene and formation of ethylene on the model system. DFT calculations were performed at B3LYP-D3/6-31G(d,p) + SDD(f,g) on Au. Toluene was represented with the PCM. Free energies are in kcal mol^{-1}. Optimized structure of the proposed intermediates **15** and **17** are shown. Non-CH_2 H atoms as well as front facing TfO^- in **17** are omitted for clarity. Selected bond distances [Å] and angles [°] for **15**: Au–CH_2 1.906, Au–O 2.281,[30] Au–P 2.403; H_2C-Au-O 144.2, H_2C-Au-P 139.7, O-Au-P 76.1; and **17**: Au–CH_2 2.079, Au–Au 2.983, CH_2–CH_2 2.461, Au–O 2.222, Au–P 2.406; H_2C-Au-O 100.5, H_2C-Au-P 98.4, O-Au-P 87.9.



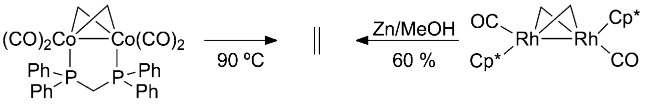
Scheme 4. Activation of complex **9** with TMSOTf. Yields determined by GC-FID.

gold carbenes generated by retro-Buchner reaction (decarbenation).[27]

The possible reaction mechanisms leading to cyclopropanes and the kinetically unusual formation of ethylene were examined on a model system by means of DFT calculations (Figure 3). Initially, a purely dissociative mechanism analogous to the proposed formation of carbenes from carbenoids of Pd[28] and Ni[29] was considered. Complete dissociation of the triflate anion from the activated carbenoid **12** leads to the formation of a gold methylidene **13** from which cyclopropanation of norbornene can occur without an apparent barrier (Supporting Information, Figure S31). This scenario is however unlikely as the energy required to split a neutral molecule into two charged species is prohibitively high (70.9 kcal mol^{-1}). Nevertheless, a species corresponding to cationic [(JohnPhos)AuCH$_2$]$^+$ could be experimentally detected upon ESI-MS of **1a**, suggesting that in sufficiently energetic conditions gold(I) carbenes can be accessed from stable carbenoids.

Cyclopropanation can alternatively occur via a three-centered transition state **TS-I**, in analogy to the Simmons–Smith reaction,[31] leading to [LAuOTf] (**14**) and cyclopropane **4b** (Figure 3). This pathway is energetically accessible and can be considered competent for the formation of cyclopropanes. Alternative mechanisms involving reductive elimination from metallacyclobutane[32] structures were also considered but found to be unlikely (Supporting Information, Figure S33). No path for the formation of ethylene from two carbenoids **12** could be located. It should be noted that, to the best of our knowledge, no homocoupling of a Simmons–Smith carbenoid has been reported to date. Ethylene most probably arises from the coupling of two bridging methylene units in a dimeric structure as originally proposed for Re[22] and Sc[33] methylidenes and found experimentally in well-characterized Co[34] and Rh[35] complexes (Scheme 5).

To reach the analogous dimeric structure **17** (Figure 3), from which ethylene can be generated with a low energy barrier over transition state **TS-IV**, we propose the involvement of the neutral gold carbene **15**. This species can be formed by migration of the triflate anion from the carbon atom to the gold center via **TS-II**. Intermediate **15** exhibits a distorted trigonal planar geometry around gold center and a short Au–CH$_2$ bond length (1.906 vs. 2.087 Å in **12**). Triflate remains coordinated to gold as evidenced by the Au–O distance (2.281 vs. 2.101 Å in **14**). Three-gold(I) complexes bearing two neutral ligands and one halogen are known and have been structurally characterized.[36] The analogous species **15b** could be located using the complete JohnPhos ligand and despite the increased steric demand imposed by the full ligand **15b** lies only 28.8 kcal mol^{-1} above the parent carbenoid **7a** (Supporting Information, Figure S35). Carbene **15** can react with one molecule of carbenoid **12** to yield the Au^{I}–Au^{III} dimer **16** without an apparent barrier by a formal oxidative addition.[37] The Au^{I} center in this intermediate can perform an intramolecular S$_N$2 type attack on the CH$_2$OTf moiety bound to the Au^{III} center over **TS-III**, yielding **17** in a second oxidative addition step. Since the formation of **15** (RDS according to our calculations) and the ethylene extrusion are both unimolecular reactions, the experimentally observed first order decay of **7a** can be rationalized in terms of our proposed mechanism. The difference in activation energies for cyclopropanation and ethylene formation processes accounts for the observed reactivity pattern, while cyclopropanations can be performed at very low temperatures, ethylene generation only reaches completion after more than one hour at room temperature.



Scheme 5. Reported formation of ethylene from well-characterized dimeric complexes of Co[34] and Rh[35] containing two bridging methylene units.

In summary, we have developed a simple method for the preparation of well-defined gold(I) carbenoids [LAuCH$_2$Cl] that, upon activation with a chloride scavenger, exhibit the reactivity expected from gold carbenes in solution, that is, homocoupling, olefin cyclopropanation, and Buchner reaction. We expect these complexes to become a useful tool for the examination and mechanistic understanding of processes involving gold carbenes in solution, particularly elusive methylidenes, which have been so far primarily studied in the gas phase.

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Conflict of interest

The authors declare no conflict of interest.

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