Gold Complexes | Hot Paper

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β- and α-Hydride Abstraction in Gold(I) Alkyl Complexes**

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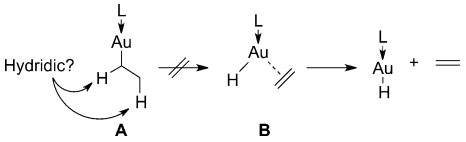
Dedicated to Professor Helmut Schwarz on the occasion of his 70th birthday

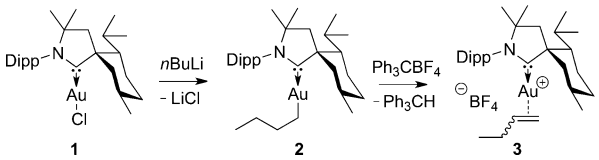
β-hydride elimination is a process commonly encountered for alkyl metal complexes.[1] In contrast, α-hydride elimination, which generates a metal–hydrido–carbene complex, is far less common.[2] Both processes require the availability of an empty orbital on the metal.[3–5] Recently, Köppel, Hashmi, and co-workers studied, experimentally and computationally, the thermally induced β-H elimination reactions of d^{10} gold(I)-alkyl complexes **A** (Scheme 1).[6] They concluded



Scheme 1. Unfavored β-hydride elimination from a gold(I) alkyl complex.[6]

that such a process, leading to a gold(I)–hydride complex and free alkene, is precluded by the high energy of the three-coordinate gold(I)–alkene–hydride complex **B**, which is due to the filled d-shell of gold(I). On the other hand, β- and α-hydride abstractions from alkyl metal complexes, yielding metal–alkene and metal–carbene complexes, respectively, are processes that have been well-developed.[7] However, none of these reactions are known with gold complexes. To provide more insights into these elimination or abstraction processes, we decided to probe the hydricity of the β- and α-hydrogen atoms of gold(I) alkyl complexes. Herein we show that both reactions, leading to gold(I)-alkene and gold(I)-carbene complexes, are feasible.

To favor the abstraction of a hydride from gold(I) alkyl complexes, we chose a very electron-donating ancillary ligand, namely a cyclic (alkyl)(amino)carbene (CAAC).[8–10] CAAC gold(I)–*n*-butyl complex **2** was prepared in high yield (97%) from the CAAC gold(I) chloride **1** by simple ligand exchange with *n*-butyllithium (Scheme 2). In the $^{13}C\{^1H\}$ NMR spectrum of complex **2**, the carbene peak shifted drastically downfield (**2**: 266.8, **1**: 237.2 ppm), clearly indicating the exchange of the chloride by a more electropositive substituent. The structure of **2** was confirmed by a single-crystal X-ray diffraction study.[11]



Scheme 2. Synthesis of gold(I) *n*-butyl complex **2** and hydride elimination. Dipp = 2,6-diisopropylphenyl.

Reaction of **2** with triphenylcarbenium tetrafluoroborate in CH_2Cl_2 proceeded quickly as indicated by the fast decoloration of the reaction mixture. The ^1H NMR spectrum shows the quantitative formation of triphenylmethane, and three new multiplets at 4.8, 5.0, and 6.2 ppm that indicate the presence of a coordinated alkene (Figure 1, top). The $^{13}C\{^1H\}$ spectrum shows two carbene signals at 243.3 and 243.4 ppm. These data are consistent with the formation of two diastereomers of gold(I)–alkene complex **3** (owing to the presence of the chiral menthyl group of the CAAC ligand).

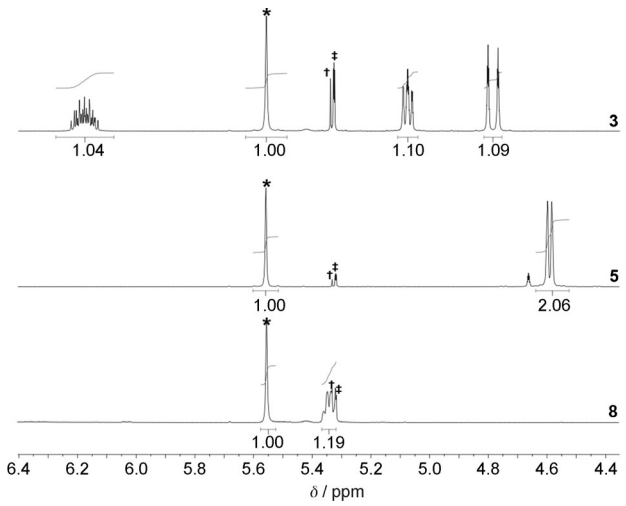


Figure 1. Expansion of the ^1H NMR (500 MHz) spectra of complexes **3**, **5**, and **8**. * = Ph_3CH; † = CH_2Cl_2; ‡ = $CHDCl_2$.

This result confirms that hydride abstraction is feasible from a gold(I) alkyl complex **A**. However, two possible mechanistic pathways can be envisioned: the typically encountered β-hydride abstraction, or an α-hydride abstraction yielding the cationic bis(carbene) gold(I) complex **D**,[12]

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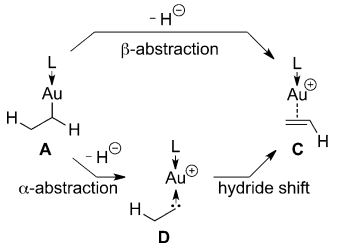
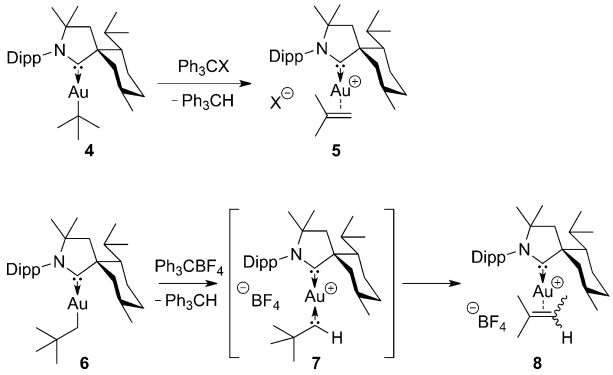
which subsequently rearranges to the gold(I)–alkene complex **C** via 1,2-hydride shift (Scheme 3).

To differentiate between these two pathways, we turned our attention to the gold(I) *tert*-butyl complex **4** and gold(I) neopentyl complex **6**, which possess no hydrogen atoms that can undergo α- and β-hydride abstraction, respectively (Scheme 4).



Scheme 3. Two possible mechanistic pathways towards the formation of gold(I)–alkene complexes.



Scheme 4. β-hydride and α-hydride abstraction from gold(I) alkyl complexes **4** and **6**, respectively.

Reaction of **4** with triphenylcarbenium tetrafluoroborate or trityl tetrakis(perfluoro-*tert*-butoxy)aluminate occurred instantaneously, and the gold(I)–alkene complex **5** was isolated in 92% yield. Two singlets at 4.58 and 4.60 ppm for the diastereotopic C=CH_2 protons were detected in the ^{1}H NMR spectrum (Figure 1, center). In the ^{13}C{^{1}H} NMR spectrum, the carbene peak shifted upfield to 242.0 ppm and two resonances were detected at 89.5 and 155.8 ppm for the CH_2 and quaternary carbon for the alkene, respectively. Single crystals were obtained by vapor diffusion of pentane into a saturated fluorobenzene solution of **5**, and the X-ray diffraction study confirmed the η^2-coordination of the alkene to the cationic gold(I) center (Figure 2, left).

Comparing the structural data for **5** to those of analogous N-heterocyclic carbene (NHC)[13] or tri-*tert*-butylphosphane gold(I)–isobutene complexes,[14] it appears that although the Au1–C2 and Au1–C3 bond distances are similar, the C2–C3 bond length of **5** is significantly lengthened (Table 1). This is most likely due to the enhanced backbonding from the gold center, which is enriched by the stronger electron donating properties of the CAAC ligand versus NHCs or phosphanes.[15]

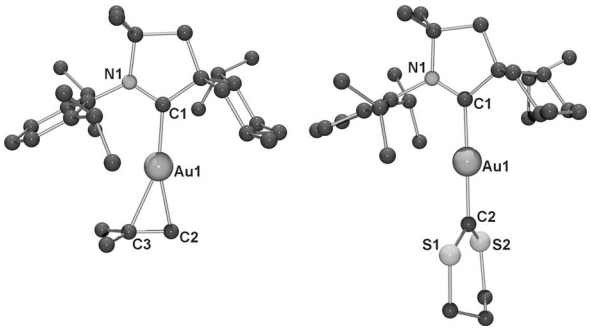


Figure 2. Structure of **5**·[tetrakis(perfluorotertbutoxy)aluminate] (left) and **10**·[tetrafluoroborate] (right) in the solid state. Hydrogen atoms and counterions have been omitted for clarity.

Table 1: Selected bond lengths [Å] for gold(I)–isobutene complexes.

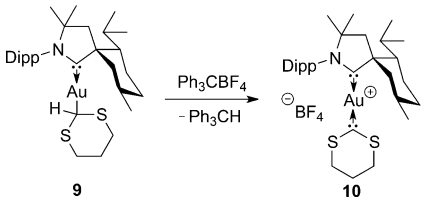
Complex	Au1–C2	Au1–C3	C2–C3
[(*t*Bu$_3$P)Au(*iso*butene)]	2.224	2.350	1.349
[(IPr)Au(*iso*butene)][a]	2.199	2.285	1.331
5	2.202	2.359	1.383

[a] IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

Reaction of the gold(I)-*neo*-pentyl complex **6** with triphenylcarbenium tetrafluoroborate was drastically slower than in the case of **4**, with full conversion of the starting material only observed after 6 h. In the ^{1}H NMR spectrum, quantitative formation of triphenylmethane was detected, as well as a broad quartet at 5.34 ppm ($J = 6.0$ Hz) (Figure 1, bottom). In the ^{13}C{^{1}H} NMR spectrum, two carbene peaks appeared at 241.6 and 241.8 ppm, and two very close new *C*H signals were detected at 107.2 ppm. These data indicate the formation of the two diastereomeric gold(I)–(2-methylbut-2-ene) complexes **8** (Scheme 4).

The latter result strongly suggest that α-hydride abstraction is possible on a gold(I) alkyl complex. Monitoring the reaction by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy did not allow for the observation of the bis(carbene) intermediate **7**, indicating that the α-elimination process is the rate-determining step of the reaction, with the 1,2-methyl shift occurring rapidly.

To confirm the formation of a carbene by α-hydride abstraction, we prepared the gold(I) dithianyl complex **9**, in which the ensuing carbene center would benefit from the well-known stabilizing effect of heteroatoms, featuring a lone pair of electrons.[16] Complex **9** cleanly reacted with triphenylcarbenium tetrafluoroborate, yielding the expected cationic bis(carbene) gold(I) complex **10** (Scheme 5). Quantitative formation of triphenylmethane, concomitant with the disappearance of the SSC-*H* signal, was observed by ^{1}H NMR spectroscopy. In the ^{13}C{^{1}H} NMR spectrum, two carbene peaks were detected at 248.0 and 268.0 ppm for the CAAC and dithianylidene, respectively. The chemical shift of the CAAC is in line with the previously reported cationic bis(CAAC) gold(I) complexes (249–252 ppm),[17] and the downfield shift for the dithianylidene[18] is consistent with its very electrophilic nature. The structure of the bis(carbene) complex was confirmed by a single crystal X-ray diffraction



Scheme 5. Synthesis of a stable cationic bis(carbene) gold(I) complex **10** by α-hydride abstraction.

study; however the quality of the crystals does not allow for discussing the geometric parameters (Figure 2, right).

These results demonstrate that while β-H-elimination is not feasible, both β- and α-hydrogen atoms of gold(I) alkyl complexes are hydridic enough to be abstracted, with the former process being easier. The α-hydride abstraction is a novel route to prepare gold–carbene complexes. The scope of this process is under active investigation.

Experimental Section

General procedure for hydride abstraction reactions: The gold(I) alkyl complex and triphenylcarbenium tetrafluoroborate (1 equiv) were loaded into a Schlenk tube. Dry dichloromethane was added, and the reaction was stirred until the bright yellow color disappeared. The solvent was removed under vacuum and the residue was washed with benzene and then pentane to remove the triphenylmethane produced during the reaction. The resulting white solid was dried under vacuum. See the Supporting Information for the full characterization of all of the compounds.

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