

The Synthesis of Gold(I) Carbene Complexes using 4-Methylthiazolylithium

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Reaction of various chlorogold(I) complexes with 4-methylthiazolylithium followed by protonation and alkylation produces new mono- and bis(carbene) complexes.

Comparatively few gold(I) carbene complexes have been prepared, the main entries into this field involving precursor isocyanide complexes,¹ cleavage of the carbon-carbon double bond in electron rich alkenes² and carbene transfer from tungsten pentacarbonyl compounds.³ We now report that various new neutral and cationic amino(thio)carbene complexes can be synthesized in satisfactory yields on addition of lithiated 4-methylthiazole to gold(I) chloride compounds and subsequent protonation or alkylation of the products formed. In this manner unique, stable amino(thio)carbene complexes which also contain phosphine, pentafluorophenyl, 4-methylthiazolyl, or chloride ligands, can be made (Scheme 1).

The synthetic pathways *a* and *b* involved simple ligand exchange (with **1**) followed by protonation and alkylation to furnish the cationic carbene complex **2** (84% yield) and the neutral aryl(carbene)gold compound **3** (70% yield) after recrystallization from tetrahydrofuran (THF).

Route *c* was followed to prepare and isolate (as a tetrabutylammonium salt) a gold 'ate' complex **4**, which could subsequently be used as an *in situ* precursor for the synthesis of neutral and cationic mono(carbene) **5** and bis(carbene) **6** complexes in high (>70%) yields.

All the reactions were, however, not straightforward. Alkylation of the 'ate' complex with MeSO₃CF₃ occurred not on the nitrogen atom as expected, but on a metal-bonded carbon atom to give **7**, which was recrystallized (THF) in 19% yield.

When the 'ate' complex, [AuMe(C⁻NCMe=CHS)]⁻, was treated with HCl, protonation of the nitrogen did occur, but in addition, the methyl ligand was also protonated and substituted by chloride to produce **8** (route *g*, 51% yield). A copper analogue of **5** could not be prepared since even protonation occurred on the coordinated carbon atom. Benzothiazolylithium reacted similarly to the title reactant.

The structures of the new compounds were based on elemental analysis (C, H and N), the appearance of molecular

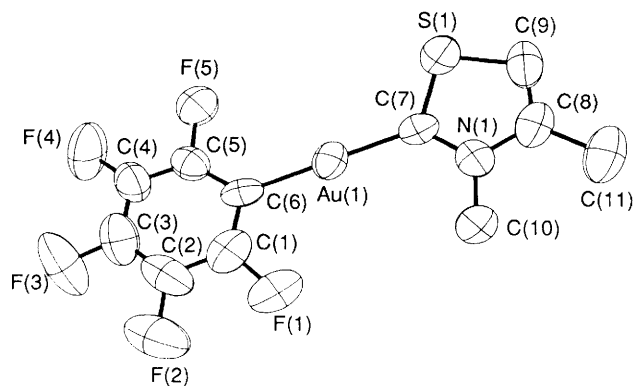
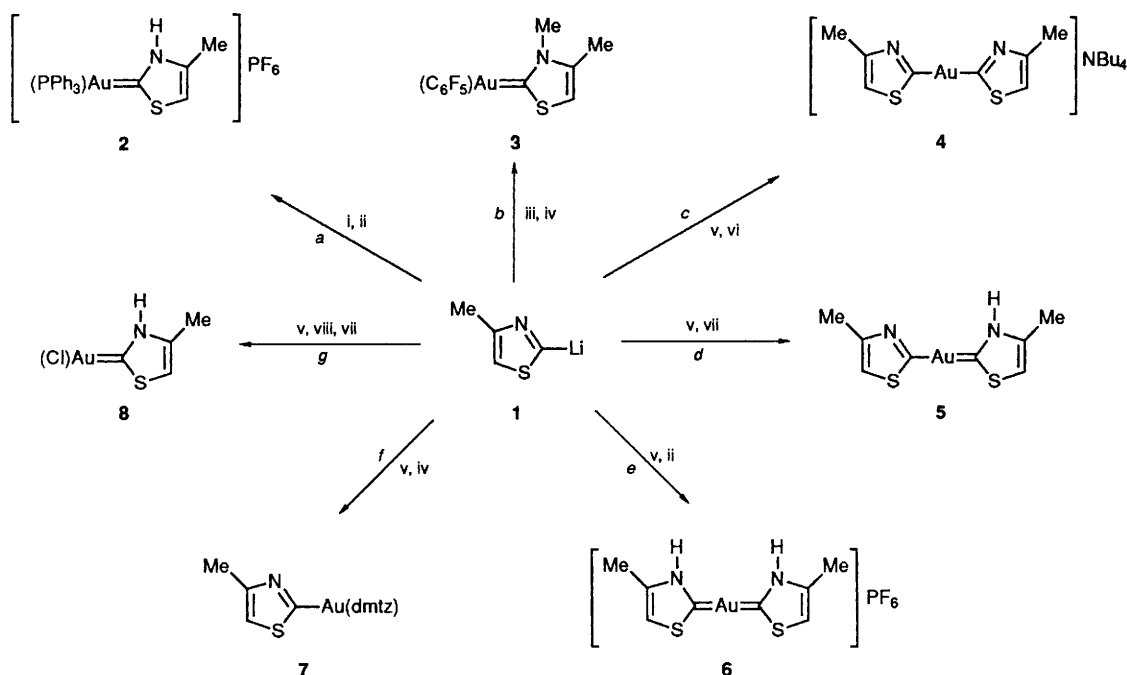


Fig. 1 Molecular structure of [Au(C₆F₅)CNMeCMe=CHS] **3**



Scheme 1 Reagents: i, PPh_3AuCl ; ii, HPF_6 ; iii, $\frac{1}{2}\text{C}_6\text{F}_5\text{Au}(\text{tht})$; iv, $\frac{1}{2}\text{MeSO}_3\text{CF}_3$; v, $\frac{1}{2}\text{ClAu}(\text{tht})$; vi, NBu_4Br ; vii, $\frac{1}{2}\text{HCl}$ (in OEt_2); viii, $\frac{1}{2}\text{LiMe}$ (tht = tetrahydrothiophene; dmtz = 2,4-dimethylthiazole)

ions of the neutral compounds in their mass spectra, NMR spectra† and a single crystal X-ray study of 3.‡

The molecular structure of the linear [angle C(6)–Au–C(7), 178.6(4)°] complex is shown in Fig. 1. The gold–aryl carbon bond of 1.993(10) Å is in accordance with such bonds in other known pentafluorophenyl complexes.⁷ The gold–carbene

carbon distance is 1.961(9) Å {compare the 2.02(3) Å separation in the carbene complex $[\text{Au}(\text{Cl})\text{C}(\text{NMe}_2)\text{Ph}]$ }.⁸ The dihedral angle between the planes formed by the two organic ligands is 5.35° and the shortest intermolecular gold–gold distance 3.95 Å.

A detailed study concentrating (i) on the use of other α -deprotonated imine compounds in carbene complex synthesis as well as (ii) on the reactivity of ‘ate’ complexes towards various insertion reactions, is in progress.

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† ^1H NMR spectra clearly differentiates between N or C alkylation. The alkylated methyl group in 3 resonates at δ 4.17 whereas the 2-methyl in 7 has a signal at δ 2.47. An unexpected feature of the ^{13}C spectra is that only small differences are found in the resonances of the metal-bonded carbons of compounds 4 (alkyl), 5 (both), 6 and 8, which all occur at δ 205 \pm 1. The carbene carbon atoms in 2 and 3 resonate at δ 184.6 and 214.5 respectively.

‡ *Crystal data:* $\text{AuC}_{11}\text{F}_5\text{H}_7\text{NS}$, $M = 477$, monoclinic, $a = 27.533(2)$, $b = 7.292(1)$, $c = 13.154(1)$ Å, $\beta = 103.92(1)^\circ$, $U = 2563.5$ Å³, $Z = 8$, $D_c = 2.47$ g cm⁻³, $F(000) = 1760$, $\lambda(\text{Mo-K}\alpha) = 0.7107$ Å, $\mu = 112.26$ cm⁻¹, space group $C2/c$. 4054 Reflections were collected on an Enraf-Nonius CAD4 diffractometer in the range $3 \leq \theta \leq 30^\circ$ and corrected for Lorentz and polarization effects and absorption. The structure was solved by Patterson and Fourier methods and refined anisotropically with a full matrix method ($1/\sigma^2 F$ -weights) using SHELX 76.⁶ All hydrogen atoms were placed in calculated positions and refined with a common isotropic temperature factor. Final $R = 0.028$, $R_w = 0.042$ for 2010 unique [$>4\sigma(I)$] reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.