

Fischer-type gold(I) carbene complexes stabilized by aurophilic interactions

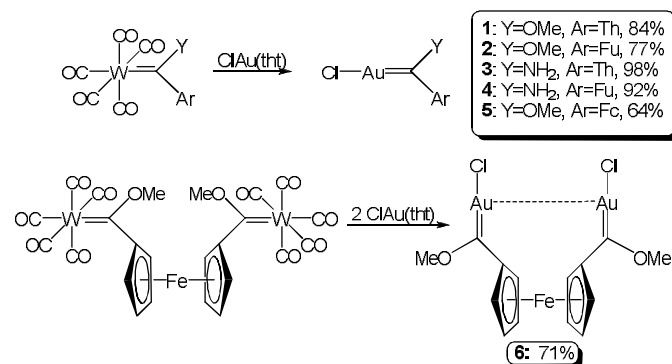
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The synthesis and structure of rare acyclic alkoxy- and aminocarbene complexes of gold(I) are reported, including a novel ferrocenophane dinuclear biscarbene complex. X-Ray diffraction analyses and DFT calculations reveal that these complexes are stabilized by genuine aurophilic interactions.

Interest in the structure of molecular gold complexes increased rapidly since 1970 due to the unexpected observation of intra- and intermolecular attractive forces between two linear gold(I) atoms.¹ Although the interaction between positively charged gold cations should result in a remarkable Coulomb repulsion, a good number of complexes with intra- and intermolecular equilibrium distances in the range from 2.50-3.50 Å has been reported.² This phenomenon, referred to as aurophilicity, opened a new arena for the structural engineering of gold compounds.³ Aurophilic bonding can be classified in three categories: unsupported, semi-supported and fully supported interactions.² Au...Au interactions can be separated by one (semi-supported) or two (fully supported) multi-atomic bridges. In the absence of such a bridge, interactions are unsupported. As stated by Gorin and Toste, the integration of theoretical and synthetic studies of Au(I) is required for deeper understanding of the fundamental properties of gold complexes in order to illuminate further avenues for study.⁴ Due to the unprecedented success of Au-N-heterocyclic carbenes, as well as acyclic diaminocarbene complexes in the field of homogeneous catalysts for organic transformations, the structures of a variety of 'prototypes' have been determined.⁵ However, examples of Fischer-type (i.e. mono-heteroatom substituted) acyclic gold(I) carbene complexes are not common.⁶ Moreover, the presence of aurophilic interactions in these complexes remains scarcely explored so far. For these reasons, we report herein a series of novel acyclic Fischer-type Au(I) carbene complexes which exhibit genuine aurophilic interactions as clearly confirmed by X-Ray diffraction and computational studies.

Following the reaction conditions reported by Raubenheimer and co-workers,^{6c} heteroaryl gold(I) chloro-monocarbene complexes **1-5** were synthesized by direct transmetalation⁷ from their tungsten(0) analogues⁸ in good to excellent yields using ClAu(tht) (tht = tetrahydrothiophene) in tetrahydrofuran (THF) at -5°C. Not unexpectedly, the ¹³C NMR spectra of the gold(I) complexes generally displayed an upfield shift of the carbene carbon atom of *ca.* 50 ppm compared to the tungsten pentacarbonyl analogues (see SI). Interestingly, the carbon

resonances for the rest of the atoms in the complexes, as well as the proton shifts, are shifted downfield, indicative of greater ring- and heteroatom involvement towards the stabilization of the electrophilic carbene carbon atom.



Scheme 1 Preparation of complexes 1-6.

Crystals were obtained by layering a THF solution of the complex with hexane at 5°C. The Au-C_{carbene} bond distances in the complexes **1-5** (Figure 1) fall within the typical range of an sp²-hybridized carbon atom bonded to a gold centre *trans* to a chlorine atom (1.96-2.02 Å).^{6e,f,9} Similar to the M-C_{carbene} bond lengths observed for their group 6 Fischer carbene counterparts,¹⁰ the carbon-gold bond distances in the methoxycarbene complexes are slightly shorter as compared to the amine-stabilized carbenes. This is due to the well-known higher π-donor ability of the nitrogen atom compared to oxygen. In all the complexes, the gold atom is linearly coordinated with the C-Au-Cl bond angle varying between 173° and 179°. Moreover, the alkoxy group of complexes **1, 2, 5** and **6** adopts the so-called *anti*-conformation,¹¹ where the methyl group is oriented towards the transition metal analogously to group 6 Fischer alkoxy carbene complexes.

Apart from that, an important feature is exhibited by complexes **1-5** in the solid state, namely they present, with the adjacent molecule,¹² Au...Au distances in the range from 3.093 to 3.307 Å. This agrees with the classification of unsupported Au-Au interaction for these species.² In complexes **1** and **2** each gold centre participates in two such interactions (as indicated in Figure 1) thus infinite chains of linked molecules are formed.

Taking into account this finding, we decided to prepare the novel ferrocenophane dinuclear biscarbene complex **6** (see Scheme 1), where the ferrocen-1,1'-diyl bridge should enforce a closer proximity between the gold atoms. Indeed, for complex **6**, a shorter Au...Au distance was found in the solid state (3.035 Å, Figure 1), thus confirming the semi-supported type of aurophilic interaction for this complex.

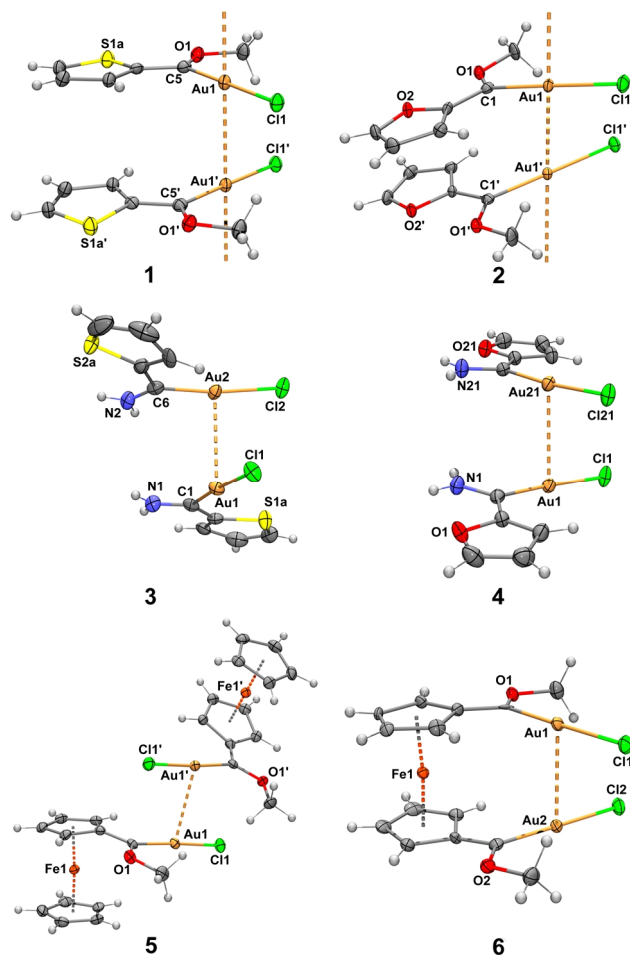


Fig. 1 Ortep/PovRay diagrams of **1-6** with adp ellipsoids shown at the 50% probability level. For **3**, a third molecule has been omitted. Au...Au interactions (Å): **1** 3.28083(11); **2** 3.3073(2); **3** 3.2179(7); **4** 3.0925(2); **5** 3.2885(2); **6** 3.0354(10). Au-C_{carbene} bond distances (Å): **1** 1.970(4); **2** 1.974(3); **3** 1.985(6), 1.984(5); **4** 1.979(3), 1.977(3); **5** 1.977(3); **6** 1.970(7), 1.960(6).

From the above structural study, it becomes clear that these novel gold(I) carbene complexes are stabilized by aurophilic interactions. To gain more insight into the nature of the Au...Au interaction in these species, Density Functional Theory (DFT) calculations were carried out using the dispersion-corrected M06 functional (M06/def2-TZVP level)¹³ on the unsupported and semi-supported complexes **2** and **6**.¹⁴ As shown in Figure 2, the computed Au...Au distance for complex **2** in the gas-phase (3.319 Å) concurs very well with the experimental distance in the solid state (3.307 Å). However, the agreement is not that good for complex **6**, very likely due to packing forces in the solid state. Despite this, the computed Au...Au distance in the latter compound is clearly shorter than in complex **2**, as a consequence of the semi-supported Au-Au interaction in this species.

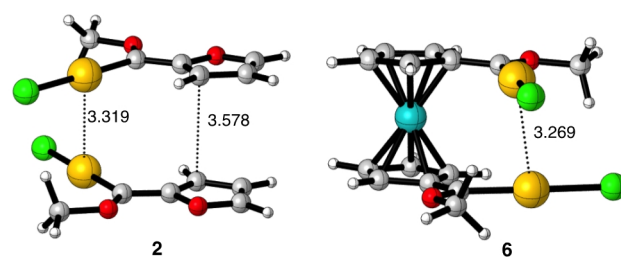


Fig. 2 Optimized (M06/def2-TZVP level) structures of complexes **2** and **6**. Bond distances are given in angstroms.

The nature of the Au...Au bonding in complexes **2** and **6** was analysed with the help of the Atoms in Molecules (AIM) and Natural Bond Orbital (NBO) methods.¹³ As depicted in Figure 3, the AIM method clearly reveals for both compounds the occurrence of a bond critical point (BCP) located at the midpoint between the two gold(I) atoms which is associated with a bond path running between these two atoms. These topological analyses therefore confirm the existence of an interaction between the Au(I) atoms. The computed electron density (ρ) and ellipticity (ϵ) values at the Au...Au BCP's are

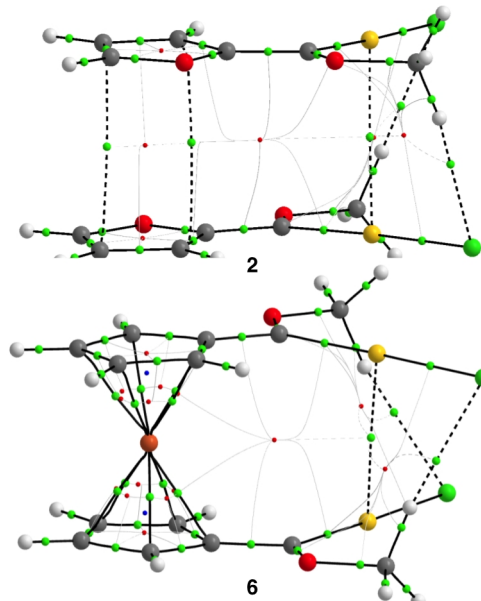


Fig. 3 AIM analyses of complexes **2** and **6**. BCP's are shown as green spheres.

similar in both complexes ($\rho = 0.014 \text{ e } \text{Å}^{-3}$, $\epsilon = 0.029$ vs $\rho = 0.013 \text{ e } \text{Å}^{-3}$, $\epsilon = 0.028$ for **6** and **2**, respectively) thus indicating a similar type of interaction. In addition, the corresponding Au-Au Wiberg Bond Index (0.14 and 0.15 for **2** and **6**, respectively) are also similar and comparable to the values found for related (NHC)AuCl dimers.¹⁵ Interestingly, the Second Order Perturbation Theory (SOPT) of the NBO method indicates that the aurophilic interaction is characterized by the donation of electron density from a doubly occupied d atomic orbital of one Au(I) to an empty p atomic orbital of the adjacent metal (see Figure 4). The associated SOPT energy computed for **2** and **6** is quite remarkable ($\Delta E^{(2)} = -9.4$ and -9.3 kcal/mol, respectively), thus reflecting the importance of these aurophilic interactions in the global

stabilization of the novel Fischer type Au(I)-carbene complexes described herein.

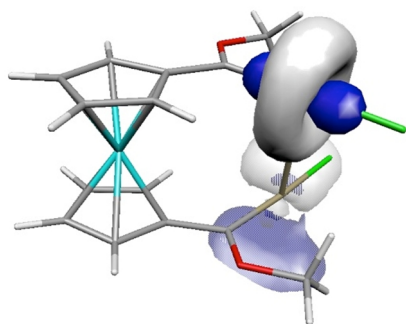


Fig. 4 NBO-molecular orbitals responsible for the Au...Au interaction in complex 6 (isosurface value of 0.035 au).

In summary, uncommon examples of Fischer-type gold(I) carbene complexes are prepared by direct transmetalation reaction from their corresponding tungsten(0) carbene complexes and ClAu(tht). By means of X-ray diffraction analyses and DFT calculations, stabilizing aurophilic interactions in Fischer-type carbene complexes are characterized for the first time. Indeed, the Au...Au interaction allows the preparation of the first Fischer-type ferrocenophane biscarbene complex containing two Au(I) atoms. Further work aimed at the preparation and reactivity of related (semi)supported carbene complexes exhibiting aurophilic interactions is in progress in our laboratories.

Acknowledgements

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic procedures and analytical data; data tables for single crystal X-ray structural analysis; Computational details and Cartesian coordinates and energies for the optimised compounds **2** and **6**. CCDC numbers for complexes **1** – **6**: 962460, 962459, 962461, 963795, 962458 and 962457. See DOI: 10.1039/c000000x/

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