Dinuclear planar chiral ferrocenyl gold(I) & gold(II) complexes†

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Oxidation of Au(I) in the presence of Fe(II) allowed for the synthesis of unique dinuclear ferrocenyl Au(II) complexes via the first reported enantiopure planar chiral ferrocenyl Au(I) complex. (Spectro)electrochemical studies show that oxidation at Fe(II) is favoured, but DFT studies suggest that the energy differences for oxidation of one or the other metal should be quite small.

Metallocene based palladacycles are established as catalysts for asymmetric synthesis enabling a number of catalytic asymmetric applications, for which no other catalyst has surpassed. Related metallacycles, like the corresponding platinacycles, have been less studied, but recently they also demonstrated high potential as carbophilic catalysts. In contrast, planar chiral enantiopure ferrocenyl gold complexes are not known so far and only a few achiral or racemic complexes have been reported. In addition, one planar chiral ruthenocenyl Au(II)PPh₃ complex has been reported, but isolation of pure material was not achieved.

Due to the lack of metallocenyl gold complexes, little is known about their reactivity. Based on the many applications of Au(I) catalysts and the catalytic efficiency of metallocene based metallacycles, the study of metallocenyl gold complexes has attracted our interest. This report puts forward the first case for the asymmetric synthesis and structural elucidation of planar chiral ferrocenyl Au complexes including auracycles featuring Au(II) centers involved in short Au–Au bonds.

Our targets were ferrocenyl Au complexes in which phosphines as additional ligands would be avoided as they might impede future catalytic applications by their high affinity to Au. ortho-Lithiation of 1 and subsequent trapping with (Me₂S)AuCl proceeded smoothly and gave the dinuclear Au(I) complex 2 with high diastereoselectivity in good yield (Scheme 1).

X-ray analysis of 2 shows a tetranuclear solid state structure (Fig. 1, left), in which two dinuclear complexes containing a bridging pair of anionic C,N-ligands are connected via an intermolecular Au(I)···Au(I) interaction (separation: 3.0651(3) Å). The Me₂S-ligands have been replaced by oxazoline N-donors resulting in a head-to-tail ligand arrangement to form helically chiral 10-membered rings featuring intramolecular Au(I)···Au(I) interactions (distances: 2.8449(3) & 2.8452(3) Å). The ¹H-¹³C-NMR
Epimerisation thus appears to be promoted by the Au source, but is also observed in CDCl₃ solutions containing traces of DCl.

In addition, isomerically pure 3 can also be formed simply by heating a solution of 2 in CH₂Cl₂ under N₂ for several days in a closed vial. Dichloromethane thus also serves as the oxidising agent (eqn (1)).¹⁷,¹⁸ In contrast, trials to oxidise 2 by different silver salts just resulted in decomposition.

Cyclic voltammetry (CV) and spectrophotometric (SEC)¹⁹ properties for 1, 2 and 3 were studied to get more insight into their redox behaviour. The ligand (1) redox is highly reversible and consistent with a ferrocene/ferrocenium (Fe²⁺/) couple (ESI†). The CVs for 2 and 3 both contain two e⁻ reversible oxidations separated by 137 mV and 160 mV, respectively. The processes for 2 are anodically shifted by an average of 135 mV compared to 3, which is consistent with the overall higher oxidation state of the Au(i) species.

The voltammogram of 2 also contains an irreversible oxidation at 0.9 V vs. Fe₀²⁺. While 3 does not have this irreversible oxidation, the CV does have an irreversible reduction wave at ~1.2 V vs. Fe₀²⁺ (ESI†). Due to the relatively high potentials and irreversible nature of these processes they are associated with the direct oxidation and reduction of the Au centers, respectively.

The two reversible processes in the CV for 2 and 3 could be differentiated in the UV-Vis-NIR SEC (Fig. 2). The in situ oxidation of 2 to 2⁺ resulted in the growth of an absorption band at 475 nm, and a lower energy band at 660 nm. The second oxidation, 2⁺ to 2²⁺, results in the quenching of the band at 475 to a lower energy band at 660 nm. The two reversible processes in the CV are therefore the oxidation of the iron in the ferrocene moiety. The strength of the band in the UV-Vis-NIR and the separation of the oxidation events in the CV indicate weak communication between the ferrocene moieties.²⁰

The UV-Vis-NIR SEC for the two oxidations of 3 contains only the shift of the band at 544 nm to a lower energy band at 586 nm, the second oxidation also shifts the band to a lower energy at 615 nm. The spectra are consistent with ferrocenium.

As shown above, chemical formation of the Au(i) species is selectively possible without affecting the ferrocene core. Both solid 3 and 3ʹ proved to be quite stable towards air and moisture, as no decomposition was observed in air after several weeks at 22 °C. The deep purple colour of 3/3ʹ in solution is quite uncommon for ferrocene derivatives.²¹ Known dinuclear aryl Au(i) complexes display bands in the range of 356–416 nm, which have been interpreted to originate from the Au(i)–Au(i) bonds.¹⁵ The intense purple colour of 3/3ʹ in solution probably...
results from d–d iron transitions and displays the electron-withdrawing character of the Au(n) centers. The latter might also facilitate the observed partial epimerisation of the planar chiral ferrocene entities in the presence of an excess of carboxylic Au(i) or DCl.22 We assume that the Au source and the Brønsted acid interact with the CpFe fragments (like in π-complexes) and thus promote the reversible CpFe decomposition from the disubstituted Cp ligands.

For a computational analysis, the crystal structures of 2 and 3 as well as of (Me₅S)AuCl have been optimised using the Kohn–Sham density functional theory (DFT) at the TPSS¹¹ level of theory with Grimme’s D3 dispersion correction²⁴ using the def2-TZVP²⁵ basis set in the TURBOMOLE program package.²⁶ Solvation in diethylether was modelled using the COSMO continuum solvation model.²⁷

For a better understanding of the reactivity of 2, the Kohn–Sham orbitals of the structure were analysed. The theoretical justification of the interpretation of eigenvalues in terms of approximate orbital energies has very recently been worked out by Chan et al.²⁸ The HOMO down to the HOMO–6 of 2 lie quite tightly together between −4.12 eV and −4.81 eV (ESI†) and are located either on both gold and iron atoms or on the iron atoms, showing that gold and iron centers are in principle both prone to oxidation.

Intrinsic Bond Orbitals (IBOs)²⁹ were calculated using the same parameters as for the calculation of the Kohn–Sham orbitals using the Molpro program package.³⁰ IBOs have the advantage of reliably yielding an orbital picture in terms of Lewis structures, best suited for chemical interpretation.²⁹,³¹ IBO analysis of the C–Au bond in 2 and 3 exhibits a distinct polarisation towards the C atom. Only 0.584 (i.e. 27%) and 0.743 (37%), respectively, of the bond charge is located on the gold atom. Furthermore, the difference of these charges is an indicator for the electron-withdrawing character of the Au centers after oxidation to Au(n) in 3. Whereas in 2 no covalent character in the Au···Au interaction can be observed through the IBO analysis (the interaction evidently is of pure aurophilic³² character), the Au–Au bond in 3 has a clear σ character (Fig. 3). Interestingly, the Au–Cl bond in 3 is partly located on the remote gold atom (respective location of the bond on the centers of the Cl–Au–Au axis: 83%, 8%, and 7%), which can be interpreted as a strong contribution of an α···M effect from the Cl atom towards the Au–Au moiety (see Fig. 3).

This clearly indicates a strong electronic cooperation of the two gold centers. Hashmi et al.³⁴ very recently showed that IBO locations on atomic centers correlate very well with electrophilic substituent constants (Hammett parameters),³⁵ which encouraged us to deduce bond stabilities from IBO partial charges. The Au–N bond has a clear dative character in both 2 and 3, since it is chiefly located on the ligand (87% and 86% of the bond respectively). For comparison, in the dative S–Au bond of (Me₅S)AuCl 79% of the bond is located on the ligand. Kohn–Sham orbitals and IBOs of the optimised geometries have also been calculated with three other DFT functionals (TPSSH, PBE³⁶ and PBE0), without deviating from the conclusions that have been drawn from the results using the TPSS functional.‡

We have reported the first asymmetric syntheses of ferrocenyl gold complexes. A dinuclear Au(i) complex featuring two bridging monoanionic C,N-ligands was generated by diastereoselective ortho-lithiation and trapping with (Me₅S)AuCl. A ten-membered helically chiral (N–C–C–C–Au)₃ ring was formed, which contains aurophilic Au(i)···Au(i) interactions. The latter might facilitate the smooth oxidation to the corresponding dinuclear auracyles featuring a short Au(n)···Au(n) bond. While the helical chirality and the head-to-tail ligand arrangement are conserved in the Au(n) species, we noticed a partial epimerisation of one ferrocene fragment, which seems to be caused by excess of (Me₅S)AuCl. The latter also acts as the oxidising agent, but even CH₂Cl₂ can be applied demonstrating the ease of oxidative additions to this kind of Au(i) species. This might create possibilities for Au(n) catalysis, which is currently investigated in our laboratory. While (spectro)electrochemical studies show that there is a preference for oxidation at Fe, the theoretical studies suggest that the energy gaps between the highest molecular orbitals are quite small and that the latter are located either mainly on Fe, or on both Fe and Au.

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Notes and references

‡ For the complete data set of computational results and for a more detailed discussion of the parameters used and tested in the calculations we refer to the ESL.†

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