Gold Complexes

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Gold(I)-1,3-Diene Complexes: Connecting Structure, Bonding, and Reactivity**

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alkenes · gold · homogenous catalysis ·
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Gold is a very special element, as noted, for example, by Johann Wolfgang von Goethe, who wrote in Faust I, verse 2802 ff.: “*Nach Golde drängt,//Am Golde hängt//Doch alles.*” [“Toward gold throng all//To gold cling all.” English Translation by George Madison Priest] This expression may currently be transferred to gold catalysis;[1] in July 2011 3583 hits were found for gold catalysis when searching the Web of Science. Review articles that received more than 3000 citations are available and clearly show the perspective for this type of catalysis. Out of the multitude of possible transformations catalyzed by Au^I, the fundamentals of the hydroamination reaction of dienes catalyzed by $\{R_3PAu\}^+$ were recently investigated by C. Russell and S. McGrady.[2] Herein we aim to put this work into a wider perspective.

In many aspects Gold is unusual: it holds the record for electronegativity of a metal, the Pauling electronegativity, $\chi_P(Au)$, is as high as 2.54 and thus close to that of C (2.55) or H (2.20) and very different to the properties of its lighter homologues Cu and Ag (Table 1). However, the Mulliken–Jaffé (and other) electronegativity scales disagree with this high value and give much lower values (Table 1). Still gold is capable of forming true Au^- salts,[3] such as Cs^+Au^-, highlighting the capability of Au to attract electrons (cf. electron affinity (EA) in Table 1). Moreover it is a true carbon Lewis acid that prefers coordination to soft carbon-ligands rather than many of the more electronegative elements. Additionally its chemistry is strictly orbital controlled, very covalent and strongly influenced by relativity that largely contracts the 6s atomic orbital (AO; or a combination of the 6s and the by relativity destabilized $5d_{z^2}$ AO) making it perfectly suited for flexible orbital-based interactions.

Table 1: Fundamental properties of gold in comparison to its lighter homologues copper and silver, as well as hydrogen.

Element	χ (Pauling/Mulliken–Jaffé[a])	IE [eV]	EA [eV]	*d*(M−C) [pm][b]
Cu	1.90/1.49	7.73	−1.24	214.7(8)
Ag	1.93/1.47	7.58	−1.30	239.6(5)
Au	2.54/1.87	9.22	−2.31	226.8(5)
H	2.20/2.25	13.60	−0.75	–

[a] Electronegativity of the *n*s-orbital ($n=1, 4, 5, 6$); [b] in the isostructural $[M(\eta^2\text{-}C_2H_4)_3]^+[WCA]^-$ complexes ($M=Cu$, Ag: $WCA=[Al\{OC(CF_3)_3\}_4]$;[4,5] $M=Au$, $WCA=[SbF_6]$[6]).

In coordination chemistry, Au^I often forms linear 14 valence electron (VE) complexes of type $[L\text{-}Au\text{-}L]^+$ ($L=$ soft donors of the hard soft acid base (HSAB) concept) that may be viewed to include Au as sd-hybridized. But what about simple Au^I-organometallic complexes? In contrast to Cu and Ag, Au^I forms thermally stable gold carbonyls that are exclusively σ-bonded as indicated by the unusually high CO stretching frequency of the linear $[OC\text{-}Au\text{-}CO]^+$ of 2254 cm^{-1} (Figure 1).[7] This value is considerably higher than in free CO (2143 cm^{-1}) and demonstrates that there is no back-bonding contribution from the Au side. There is no evidence for the existence of any higher Au^I carbonyls, such as $[Au(CO)_3]$ or $[Au(CO)_4]^+$.

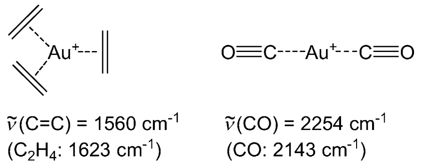

Figure 1. Simple organometallic complexes of Au^I and their principal experimental vibrational frequencies[6,7] as an indicator for the bonding situation in the complex.

When turning to the simplest alkene as a ligand, ethene, an η^2-bound planar spoke-wheel-structure was realized in $[Au(\eta^2\text{-}C_2H_4)_3]^+$ with the classic $[SbF_6]^-$ counterion[6] and in subsequently also with $[Al(OC(CF_3)_3)_4]^-$. In these cases the slightly red shifted C=C stretch indicates the possibility of some back bonding from gold orbitals to the ligand (Figure 1). No experimental evidence for a linear $[Au(\eta^2\text{-}C_2H_4)_2]^+$ was found. According to charge-density studies,[5] the bonding within the $\{Au(\eta^2\text{-}C_2H_4)\}$ moieties is best described as covalent and it includes two separate Au−C bond paths with bond critical points (BCPs) at 0.57 e^- Å^{-3} and a AuC_2 ring critical point at 0.56 e^- Å^{-3}. Thus, some weak back bonding is

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also present in the $[Au(\eta^2\text{-}C_2H_4)_3]^+$ complex and a trigonal-planar coordination of gold is preferred within the environment of three simple, non-stabilized alkenes.

But what about the possible structures of the $[R_3PAu(1,3\text{-diene})]^+$ complexes of relevance for the hydroamination reaction? From first principles, the three bonding modes shown in Figure 2 a–c may be expected.

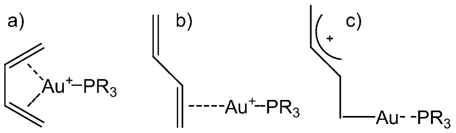
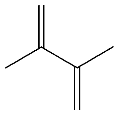


Figure 2. a–c) Principle bonding modes for the interaction of a simple 1,3-diene with a cationic $\{R_3PAu\}^+$ moiety.

The stability of modes (a)–(c) in Figure 2 will clearly be influenced by the substitution pattern at the 1,3-diene. If the carbon-centered charge in Figure 2c can be stabilized by electron-donating $+M$ ligands at the diene, mode (c) is likely to be favored over (a) and (b). However, experimental knowledge on such bonding situations was scarce[8] until the recent combined experimental and computational work by Russell and McGrady.[2] To change the electronic situation around the diene, these authors chose the three model dienes **1**–**3** and investigated their coordination to $\{R_3PAu\}^+$.



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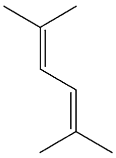

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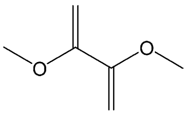


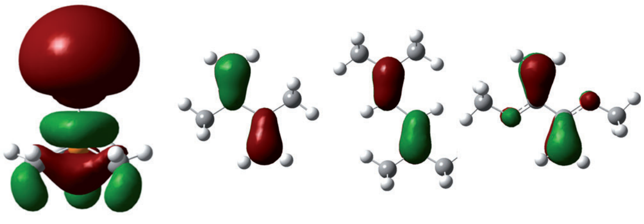
3

They tested the catalytic activity of the $[R_3PAu(\text{diene})]^+[SbF_6]^-$ salts for the standard hydroamination reaction of the diene with benzylcarbamate in 1,2-dichloroethane and in the presence of 10 mol% of catalyst. While **1** and **2** underwent hydroamination with mild conditions to form an allylic amine, the usually more reactive substrate **3** did not react at all.

Next single crystals of all three $[R_3PAu(\text{diene})]^+[SbF_6]^-$ salts were grown and analyzed by X-ray diffraction. It was found that the η^4-structure in Figure 2a was never realized. For **1** and **2** an η^2-structure slipped by about 8% towards the outer C-atom was found (cf. Figure 2b). With **3** as a ligand this slippage was far more pronounced leading to a structure that is best described as η^1 as in the limiting case presented in Figure 2c (45% slippage; Au–C bonds at 218 pm (for the coordinated C atom) and 254 pm (for the noncoordinated C atom)).

But what is the molecular origin for these differing structures? The DFT calculations by Russell and McGrady on model $[(1,3\text{-diene})Au\text{-}PMe_3]^+$ complex cations support the observed asymmetric slippage from η^2 (**1**, **2**) towards η^1 (**3**) on theoretical grounds. Since Au^I chemistry is mainly orbital controlled, we were interested to investigate, if this structural preference may be understood on the basis of simple frontier-orbital considerations. Therefore we optimized the structures of **1** to **3** as well as $\{Me_3PAu\}^+$ at the BP86/SV(P) level (Au: SDD 60 VE ECP) and analyzed their Kohn–Sham-frontier orbitals (Figure 3).

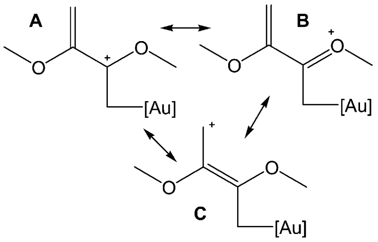
From Figure 3 it becomes apparent that for symmetry reasons, the acceptor LUMO orbital of the $\{Me_3PAu\}^+$ cation is perfectly suited to attack only one of the two π-orbitals of the C=C double bonds available for coordination (different phases of the π-lobes pointing to the acceptor). Note that this also holds for the *cis*-isomer. In contrast, if three independent alkenes, as in the $[Au(\eta^2\text{-}C_2H_4)_3]^+$ complex, interact with a central gold atom, the three π-donor orbitals of the alkenes form a set of ligand group orbitals, the lowest of which always has the same phase of the orbital pointing towards the central 6s acceptor orbital. Thus, in an arrangement of three independent alkenes, such a trigonal spoke-wheel arrangement is possible. However, when a 1,3-diene interacts with the acceptor orbital of the $\{Me_3PAu\}^+$ cation, the two independent π-orbitals of the C=C double bond must have opposite phases (Figure 3) and, regardless of the substituents, a trigonal $[(\eta^4\text{-diene})Au(\eta^1\text{-}PR_3)]^+$ arrangement is impossible owing to the nature of the frontier orbitals. Also the slippage of the structures formed, from an ideal η^2-coordination with the $\{Me_3PAu\}^+$ cation, is prearranged by the nature of the HOMO donor orbitals of the 1,3-diene: in **1** and **2** the coefficients at the outermost atoms C^A and C^D of the $(C^A{=}C^B)\text{-}(C^C{=}C^D)$ series are a bit larger inducing the 8% slippage of the $Au\text{-}(C^A{=}C^B)$ interaction. In **3** this effect is more pronounced, favoring the slippage that now reaches 45%. Moreover, in a way, Au^+ behaves as a large proton: By η^1-attack of C^A the positive charge is formally transferred to C^B (resonance structure **A**). In contrast to **1** and **2**, such an arrangement can be stabilized by back donation (resonance structures **B**/**C**) from the lone-pair orbital at the oxygen atom of the OMe group, leading to a further stabilization of the η^1-interaction with diene **3**.



$\{Me_3PAu\}^+$ LUMO	HOMO **1**	HOMO **2**	HOMO **3**
at 0.04 e^- Å^{-3}	at 0.06 e^- Å^{-3}	at 0.06 e^- Å^{-3}	at 0.06 e^- Å^{-3}
-8.115 eV	-5.613 eV	-4.823 eV	-5.169 eV

Figure 3. Kohn–Sham-frontier orbitals of the structure optimized $\{Me_3PAu\}^+$ cation and **1** to **3** at the BP86/SV(P) level (Au: SDD 60 VE ECP).

However, although this back bonding stabilizes the carbocationic charge in the complex with **3**, this interaction also leads to a higher barrier for slippage of the $\{R_3PAu\}^+$ moiety along the $(C^A{=}C^B)\text{-}(C^C{=}C^D)$ path: DFT calculations



showed that the transition state for such a slippage, that is, the coordination of the {Me$_3$PAu}$^+$ moiety to the central two C^B–C^C atoms of the diene, is 65 kJ mol^{-1} in energy higher than the η^1-ground state. The reason for this barrier appears to be that the strong C=O bond character in the ground-state structure of [R$_3$PAu(**3**)]$^+$ (d_{CO}: 132 pm, resonance structure **B**) has to be considerably weakened in the transition state structure (d_{CO} = 135 pm). In the absence of such mesomeric stabilizations, for example, in complexes with **1** and **2**, the respective transition states are more accessible and only 31 (**1**) or 44 (**2**) kJ mol^{-1} higher in energy than the respective η^2-ground state. Thus the entire system with **1** and **2** behaves more flexibly against the attack of an incoming amine nucleophile and thus more readily undergoes hydroamination.

We expect that the principles worked out in the original publication and further elaborated herein hold for many related cases. These findings again highlight the importance of orbital control for Au^I systems, either in catalysis or elsewhere.

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