LAuOH (L=L2, L3, IMes) was stud-

ied. Ligand- or base-assisted intercon-

(L2Au)₃O⁺, and L2AuOH are descri-

bed. Reactions of dppf(AuOTf)₂ and S-

tolBINAP(AuOTf)₂ with bases provid-

ed more interesting oxonium ions,

 $L8(Au)_2OH^+$, and $[L8(Au)_2]_3O_2^{2+}$, but

their exact structure was not establish-

ed. Several reactions between different

oxonium species were conducted to ob-

serve mixed heteroligand oxonium spe-

cies. Reaction of L2AuNCMe+ with

 S^{2-} was studied; several new complexes

with sulfide are described. For many

reversible reactions the corresponding

equilibrium constants were determined.

molecular composition was

 $(L2Au)_2OH^+$,

 $[dppf(Au)_2]_3O_2^{2+},$

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Coordination Chemistry of Gold Catalysts in Solution: A Detailed NMR Study

Alexander Zhdanko,^[a] Markus Ströbele,^[b] and Martin E. Maier^{*[a]}

plexes dppf(AuOTf)₂ and S-tolBINAP-

Abstract: Coordination chemistry of gold catalysts bearing eight different ligands $[L=PPh_3, JohnPhos (L2), Xphos$ (L3), DTBP, IMes, IPr, dppf, S-tolBI-NAP (L8)] has been studied by NMR spectroscopy in solution at room temperature. Cationic or neutral mononuclear complexes LAuX (L=L2, L3, IMes, IPr; X=charged or neutral ligand) underwent simple ligand exchange without giving any higher coordinate complexes. For L2AuX the following ligand strength series was determined: MeOH \ll hex-3-yne < MeCN \approx $OTf^{-} \ll Me_2S < 2,6$ -lutidine < 4-picoline < CF₃CO₂⁻ \approx DMAP < TMTU <

 $PPh_3 < OH^- \approx Cl^-$. Some heteroligand complexes DTBPAuX exist in solution in equilibrium with the corresponding symmetrical species. Binuclear com-

(AuOTf)₂ showed different behavior in exchange reactions with ligands depending on the ligand strength. Thus, PPh₃ causes abstraction of one gold atom to give mononuclear complexes LLAuPPh₃⁺ and $(Ph_3P)_nAu^+$, but other N and S ligands give ordinary dicationic species $LL(AuNu)_2^{2+}$. In reactions with different bases, LAu⁺ provided new oxonium ions whose chemistry studied: $(DTBPAu)_3O^+$, was also $(L2Au)_2OH^+,$ $(L2Au)_{3}O^{+},$ (L3Au)₂OH⁺, and (IMesAu)₂OH⁺. Ultimately, formation of gold hydroxide

Keywords: gold • ligand effects • ligand exchange • NMR spectroscopy · oxonium ions

Introduction

Gold catalysis has emerged as an extensive area of research that continues to evolve very rapidly today.^[1] However, while the arsenal of synthetic methods available to an organic chemist benefited enormously from gold catalysis, knowledge about the mechanism of the corresponding transformations remains more limited, and this area has just begun to emerge as a major topic in gold catalysis.^[2] Indeed, most papers dealing with gold-catalyzed reactions confine themselves to "proposed" mechanisms, without going into deep experimental mechanistic investigation and characteri-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201201215.

zation of the gold intermediates. Often, instead of experimental elucidation of mechanisms, computational investigations are conducted to support the mechanism.^[3]

Although general coordination chemistry of gold as a subject of inorganic chemistry has been investigated with a broad range of ligands, the coordination chemistry of gold compounds that are used nowadays as catalysts in organic transformations is largely unexplored.^[4] This actually is not too surprising, since many of them appeared after 2000.^[5] Here we present our pure coordination-chemistry investigations, which were conducted in parallel with our mechanistic studies.

The present paper describes reactions of gold complexes of the types LAuX and LAuNu⁺, where L is a strong, base or parent ligand, respectively, X is a negatively charged group in neutral complexes and Nu is a neutral weaker ligand in cationic complexes.^[6] Abbreviations, widely adopted in the text, are clear from the starting materials depicted in Figure 1. Almost all reactions were conducted in deuterated solvents (CDCl₃, C₆D₆, [D₈]THF (used pure or as a 15 vol% mixture with simple THF), CD₂Cl₂, MeOD) and were directly monitored by ¹H and ³¹P NMR spectroscopy at room temperature. Most of the reactions were conducted as NMR titrations, which allowed us to get the necessary information from changes observed in the spectra. We classify all

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Figure 1. Structures of gold complexes together with ligand abbreviations used in the text.

homoligand exchanges LAuNu⁺/Nu as "fast" if Nu gives a single set of broadened signals, and as "slow" if bound and free Nu give clear or broadened separate signals. Complexes 1 and 4-8 were prepared by reaction of the corresponding chlorides with silver triflate.

Results and Discussion

Simple ligand exchange chemistry of gold catalysts: It has long been known that Ph₃PAu⁺ (with weakly or noncoordinating anions) reacts with PPh₃ to provide mixtures of higher coordinate complexes $(Ph_3P)_nAu^+$ (n=2-4). However, individual components of the equilibria [Figure 2, Eqs. (2), (3)] could not be observed by NMR spectroscopy at room temperature because of fast exchange. The system simply gives one broadened phosphorus resonance averaged for all species.^[7] We reproduced this situation and describe it with detailed spectra in the Supporting Information. Since many of Ph₃PAu-containing complexes had been previously described, we largely focused on new species derived from other ligands. The following known species were considered of relevance for this study: Ph_3PAuNu^+ ($Nu = Me_2S$,^[8] 2,6-lutidine,^[9] 2,6-di-tert-butylpyridine, NMe₃,^[10] PPh₃), Ph₃PAuN- $(SiMe_3)_2^{[11]}$ and $(Ph_3PAu)_3O^+$.^[12]

Initially, we studied the reaction of $L2AuNCMe^+SbF_6^-$ (2) with different ligands: MeOH, hex-3-yne, Me₂S, 2,6-lutidine, 4-picoline, DMAP, TMTU, PPh₃ and Cy₃P in CDCl₃. All ligands except MeOH and hex-3-yne stoichiometrically substituted acetonitrile from 2 to give 1:1 products whose composition was established as $L2AuNu^+SbF_6^-$ [Figure 2, Eq. (4)], and in all these cases, before the equivalence point,

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Ph₃PAuOTf + PPh₃ (Ph₃P)₂Au⁺ (1) (Ph₃P)₃Au⁺ (2) (Ph₂P)₂Au⁺ + PPh₂ (Ph₃P)₄Au (3) (Ph₃P)₃Au⁺ + PPh₃ (4) L2AuNCMe⁺ + Nu L2AuNu⁺ + MeCN (5) L3AuNTf₂ + Nu L3AuNu⁺ + NTf₂ IMesAuOTf + Nu IMesAuNu⁺ + OTf (6) IPrAuOTf + Nu IPrAuNu⁺ + OTf (7) Nu = Me₂S, Lut, Pic, DMAP, TMTU, PPh₃ DTBPAuOTf + Me₂S DTBPAuSMe2⁺, (DTBP)2Au⁺,... (8) DTBPAuOTf + Lut -DTBPAuLut⁺ + OTf (9) K_{eq} $L2AuPPh_3^+ + 2 PPh_3 \implies (Ph_3P)_3Au^+ + tBu$ 0.15 L mol⁻¹ (10) L2Au(MeOH)⁺ + MeCN = L2AuNCMe⁺ + MeOH ~ 1.103 (11) / 2Au(3-hexvne)⁺ + MeCN = / 2AuNCMe⁺ + 3-hexvne 15 (12 L2AuNCMe⁺ + OTf⁻ ← L2AuOTf + MeCN ~ 2 (13) ~ 1-2·10³ / 2AuNCMe⁺ + Me₂S == / 2AuSMe₂⁺ + MeCN (14) $L2AuSMe_2^+ + Lut \implies L2AuLut^+ + Me_2S$ 26 (15) L2AuLut⁺ + Pic 📥 L2AuPic⁺ + Lut 1.7 (16) L2AuLut⁺ + DMAP → L2AuDMAP⁺ + Lut $4 - 5 \cdot 10^{2}$ (17)(DTBP)₂Au⁺ + Lut == DTBPAuLut⁺ + DTBP 4 (18) 2 DTBPAuPPh₃⁺ = (DTBP)₂Au⁺ + (PPh₃)₂Au⁺ 0.06 (19) L3AuSMe₂⁺ + Lut → L3AuLut⁺ + Me₂S 2.5 - 4(20)L3AuLut⁺ + Pic ← L3AuPic⁺ + Lut (21) 13 LL(AuOTf₂) + (>3) PPh₃ \longrightarrow LLAuPPh₃⁺ + (Ph₃P)_nAu⁺ (22) $LL(AuOTf)_2 + 2Nu \longrightarrow LL(AuNu)_2^{2+}$ (23)

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LL = dppf, S-Tol-BINAP, Nu = Lut, Pic, DMAP, TMTU

Figure 2. Equations (1)–(23) for the reactions of gold(I) complexes with nucleophiles; Lut=2,6-lutidine, Pic=4-picoline, DMAP=4-dimethylaminopyridine, TMTU=tetramethylthiourea.

MeCN gave a single broad resonance, indicating fast ligand exchange in the L2AuNCMe+/MeCN system. After the equivalence point, MeCN became completely free, giving the normal sharp signal at 2.00 ppm in the ¹H NMR spectrum. For example, in the reaction of 2 with PPh₃ the corresponding heteroligand complex L2AuPPh₃⁺ was formed as sole product, giving two doublets in the ³¹P NMR spectrum due to P-P coupling. As a characteristic feature of the ¹H NMR spectrum, the protons at the 3',5'- and 4'-positions of the biphenyl ring are significantly shifted upfield, presumably due to the influence of the inductive currents in the triphenylphosphine rings situated in close proximity. Beyond the equivalence point gradual substitution of the L2 ligand started to occur. Experimentally we found also that this process can be better described as Equation (10) in Figure 2, with an equilibrium constant of approximately 0.15 Lmol^{-1} . This demonstrates much higher preference of L2 versus the PPh₃ ligand for gold. Even 17.5 equiv PPh₃ were able to substitute only one-half of L2. Formation of stable L2AuPPh₃+

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heteroligand complex in solution was confirmed also by ESI HRMS analysis, while the presence of higher coordinate $L2Au(PPh_3)_2^+$ could not be confirmed. The absence of $L2Au(PPh_3)_2^+$ was also evident from the NMR spectra. Thus, if any appreciable amount thereof was formed in solution, it would either give new signals or shift the L2AuPPh₃⁺ signals due to the dynamic equilibrium that would be established. However, even in the presence of such a large excess of PPh₃, the resonances of L2AuPPh₃⁺ broadened only slightly and appeared at constant chemical shift, which also points to a "slow" mode of exchange in the L2AuPPh₃⁺/PPh₃ system. The significant kinetic stability of the $L2AuPPh_3^+$ complex is in sharp contrast to the behavior of the corresponding triphenylphosphine analogue (Ph₃P)₂Au⁺ and must be a consequence of increased steric hindrance of the L2 ligand. If liberated, the free L2 ligand also gave a sharp constant resonance, while an excess of PPh₃ gave a broadened resonance due to fast exchange with the partially liberated gold in the classical $(Ph_3P)_nAu^+/Ph_3P$ dynamic system [Figure 2, Eqs. (2) and (3)].

Similarly, in the reaction with Cy₃P, formation of the corresponding $L2AuPCy_3^+$ occurred, which in the presence of excess Cy₃P readily underwent substitution of L2 from gold to give $(Cy_3P)_2Au^+$ [Eq. (24)].

$$L2AuPCy_3^+ + Cy_3P \longrightarrow (Cy_3P)_2Au + L2$$
(24)

Other L2AuNu⁺ complexes with Nu=Me₂S, Lut, Pic, DMAP, and TMTU where readily obtained by reaction of 2 with the corresponding ligand; they all were completely stable in the presence of excess of ligand, giving neither higher coordinate complexes nor liberating the original phosphine ligand. For Nu=Me2S, Lut, Pic, DMAP, and TMTU, fast ligand exchange between L2AuNu⁺ and Nu was observed, but for Nu=Lut, remarkably, both free and bound forms gave separate clear resonances indicating a "slow" mode of ligand exchange, which is probably a consequence of increased steric bulk of this ligand.

Reactions of 2 with MeOH and hex-3-yne in CDCl₃ did not reveal stoichiometric substitution of MeCN, that is, the resulting complexes would be weaker than the starting one. We determined that MeOH is a weaker ligand than hex-3yne, and both are weaker than MeCN [Figure 2, Eqs. (11) and (12)]. The complex with methanol is so weak that only in pure MeOD solution (\approx 7000 equiv) does it exist as predominant form over acetonitrile. Complexes of 2 with several alkynes and alkenes were recently studied by Widenhoefer et al., and hex-3-yne exhibited the strongest binding among a range of several alkynes and alkenes.^[13] Therefore, it can be taken as a general rule for gold catalysis that binding of a cationic gold catalyst to a C=C or C=C bond of a substrate would be generally weaker than with acetonitrile by a factor of 10-100. This provides a ready explanation why acetonitrile is often not a preferable solvent for a gold(I)-catalyzed reaction: obviously, it would seriously compete with an alkyne substrate for the gold center, slowing down the overall process.^[14]

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Since gold catalysts are often prepared and used as triflates or trifluoroacetates, it was of interest to compare their binding abilities. For this purpose we prepared L2AuOTf and L2AuOTFA and found that OTf⁻ as a ligand is bound to gold slightly more strongly than MeCN [Figure 2, Eq. (13)], but more weakly than Me_2S . The OTFA salt was found to be quite strong, comparable to the complex with DMAP. This finding directly correlates with efficacy of catalysis: while triflates still provide fast reactions, the trifluoroacetates are in fact very sluggish catalysts. However, although binding of a catalyst to a substrate is important, it is not the only factor determining the efficacy of gold catalysis.

Similar studies using Me₂S, 2,6-lutidine, 4-picoline, DMAP, TMTU, and PPh₃ in CDCl₃ were conducted with $L3AuNTf_2$ (3), which displayed exactly the same properties [Figure 2, Eq. (5)]. The corresponding heteroligand complex L3AuPPh₃⁺ was formed as a sole product with triphenylphosphine, and beyond the equivalence point gradual substitution of the L3 ligand started to occur. As in the case of L2, L3 proved to be a much better ligand for gold than PPh_3 , comparable to L2, but the equilibrium constant could not be found due to signal overlaps. With Nu=Me₂S, Lut, Pic, DMAP, and TMTU the corresponding complexes L3AuNu⁺ were formed, which revealed fast L3AuNu⁺/Nu ligand exchange for Nu=Me2S, DMAP, and TMTU and slow ligand exchange for Nu=Lut and Pic. Ligand exchange in L3AuNu⁺/Nu was always slower than in L2AuNu⁺/Nu, as was evident from the line shapes, and this can be regarded as a consequence of increased steric hindrance of the L3 ligand in comparison to L2.

Then we studied reactions of DTBPAuOTf (4) having a phosphite ligand, which revealed several unexpected differences from the chemistry described above. First, 4 was found to give a heteroligand complex DTBPAuPPh₃⁺, which does not exist in individual state but undergoes reversible ligand metathesis to (Ph₃P)₂Au⁺ and (DTBP)₂Au⁺, so that all three species are simultaneously observed in solution. The equilibrium constant was estimated to be $K_{eq} \approx 0.06$ [Figure 2, Eq. (19)]. On further addition of PPh₃, DTBP is completely displaced from gold to give (Ph₃P)₂Au⁺ as a sole product. During this process higher coordinate species (DTBP)₂AuPPh₃⁺ and DTBPAu(PPh₃)₂⁺ were not detected. The homoligand complex (DTBP)₂Au⁺ was generated in the reaction between 4 and DTBP and revealed slow ligand exchange in the presence of excess DTBP. Here again, no higher coordinate $(DTBP)_nAu^+$ (n > 2) complexes were detected. One of the phosphite ligands in (DTBP)₂Au⁺ is bound rather weakly: it is already substituted by 2,6-lutidine with an equilibrium constant $K_{eq} \approx 4$ [Figure 2, Eq. (18)]. We believe that such weak binding is a consequence of both high steric hindrance and weak donor ability of the DTBP ligand. Rather in contrast with the previous chemistry, complex 4 reacts with Me₂S and TMTU to give no clear picture of what is really happening in solution. In the case of Me₂S а complex dynamic mixture of DTBPAuSM e_2^+ , $(DTBP)_2Au^+$, and $(Me_2S)_{n=1,2}Au^+$ is formed due to ligand exchange [Figure 2, Eq. (8)]. In contrast, lutidine reacted

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cleanly to give DTBPAuLut⁺ as a single product undergoing fast DTBPAuLut⁺/Lut exchange [Figure 2, Eq. (9)].

Next, IMesAuOTf (5) was treated with PPh₃ to give the expected IMesAuPPh₃⁺, which beyond the equivalence point displayed fast exchange with PPh₃. No other compounds were formed, that is, IMesAuPPh₃⁺/PPh₃ continues to be a simple binary system with PPh₃ exchange as the only process, which is not surprising, since N-heterocyclic carbene (NHC) cannot be easily substituted by a phosphine. With other ligands Nu=Lut, Pic the corresponding complexes IMesAuNu⁺ were formed, and both revealed slow IMesAuNu⁺/Nu ligand exchange [Figure 2, Eq. (6)]. Another similar NHC carbene complex, namely, IPrAuOTf (6), displayed exactly the same chemistry as 5. Ligand exchange in the IMesAuNu⁺/Nu system was found to be fast only for Nu=Me₂S and slow for other cases [Nu=Lut, Pic, DMAP, TMTU, PPh₃; Figure 2, Eq. (7)].

Further, we studied ligand-exchange chemistry of two binuclear complexes of gold. For example, when dppf(AuCl)₂ was titrated with PPh₃, the system displayed dynamic behavior with single sets of broad signals for dppf and PPh₃, but at some point sharp signals for the dppf unit were observed, together with broad signals for PPh₃ (in both ¹H and ³¹P NMR spectra), indicating formation of a single dppf complex. This can be either dppfAuCl or [dppfAuPPh₃]⁺ Cl⁻. Complex dppfAuCl was previously described and its spectra did not match those observed by as, so we suppose [dppfAuPPh₃]⁺Cl⁻ could be formed in our case. The complex [dppfAuPPh₃]⁺ was previously described as the perchlorate salt and its spectra matched those observed by us pretty well.^[15]

When $dppf(AuOTf)_2$ (7) was titrated with PPh₃, the earlystage spectra were complicated, indicating formation of a multicomponent mixture. However already at three equivalents of PPh₃, sharp signals for the dppf unit arose, together with broad signals for PPh₃ (in both ¹H and ³¹P NMR spectra), indicating formation of a single dppf complex. Similar properties were displayed by another binuclear complex, namely, $L8(AuOTf)_2$ (8). The observed behavior was clear from the NMR spectra and additionally supported by ESI MS. The observations were consistent with complete abstraction of one gold atom from the initial complex and formation of mononuclear complexes LLAuPPh₃⁺ and (Ph₃P)_nAu⁺ [Figure 2, Eq. (22)]. In case of dppfAuPPh₃⁺ the spectra matched those reported in the literature.^[15] All sharp signals (in both ¹H and ³¹P NMR spectra) were assigned to the LL unit of LLAuPPh₃⁺, and broad, time-averaged signals were assigned to a PPh₃ unit which experiences fast exchange between all the species. This also causes the phosphorus resonance of LL to appear as a singlet rather than a doublet. Formation of free LL was not observed with an excess of PPh₃, that is, while abstraction of one gold cation from the initial dicationic complex was easy, abstraction of the second gold ion is rather difficult. This might be explained by a cooperative action of both phosphorus atoms rather than the nature of each of them. Such an interaction might be described as a chelate or fast jumping of gold between the two phosphorus atoms.

In contrast to PPh₃, reactions with weaker N and S ligands revealed formation of the corresponding dicationic complexes dppf(AuTMTU)₂²⁺, dppf(AuLut)₂²⁺, *L8*(AuLut)₂²⁺, *L8*(AuPic)₂²⁺, *L8*(AuDMAP)₂²⁺, and *L8*(AuTMTU)₂²⁺, without any sign of gold abstraction [Figure 2, Eq. (23)]. Interestingly, the complexes with TMTU were slightly reactive in the presence of excess TMTU, and this suggests a further reversible unidentified process but with the equilibrium shifted to the left.

As a result of this study, the following ligand strength series was established, with some key K_{eq} values indicated (Scheme 1). Conveniently, the ligands before OTf⁻ can be



for DTBPAu⁺: DTBP < Lut IMesAu⁺: CI⁻ < PPh₃ Ph₃PAu⁺: DMAP < TMTU

Scheme 1. Ligand strength series for cationic gold complexes with some key $K_{\rm eq}$ values.

regarded as weak, from Me_2S till TMTU as moderately strong and beyond PPh₃ very strong. The range of binding affinities from MeOH till DMAP spans approximately ten orders of magnitude. During further research we were able to determine indirectly the equilibrium constant for DMAP/ TMTU exchange at Ph₃PAu⁺, which appears to be 10 in favor of TMTU. Unfortunately, it was not possible to quantitatively determine the difference in binding affinities for TMTU/PPh₃, but we suppose this may reach several (2–4) orders of magnitude.

Reaction of gold catalysts with bases: formation of LAuOH and oxonium species and their transformations: It has long been known that Ph₃PAu⁺ reacts with base and water to give triaurated oxonium salts (Ph₃PAu)₃O⁺ (9) stable in solution and in the solid state.^[12] Indeed, when proton sponge (PrSp) was added to a freshly prepared solution of Ph₃PAuOTf (1) in CDCl₃, a fast and quantitative reaction with traces of water (naturally contained in CDCl₃) occurred to give $(Ph_3PAu)_3O^+$ as the sole product [Scheme 2, Eq. (25)]. Before the equivalence point, ³¹P NMR showed a single broadened resonance indicating fast exchange in the Ph₃PAuOTf/(Ph₃PAu)₃O⁺ system. In sharp contrast, 2 reacted with proton sponge to give diaurated oxonium ion $(L2Au)_2OH^+$ (10) as a single product together with the proton sponge salt (PrSpH⁺) [Scheme 2, Eq. (26)]. Its proton spectrum exhibits a characteristic triplet at -0.42 ppm (${}^{3}J_{\text{H-P}}=1.7$ Hz) corresponding to a single OH proton. The stoichiometry of the whole reaction was deter-



Scheme 2. Reactions of gold complexes with proton sponge.

mined by integration, which showed that 1 mol of 10 is generated together with 1 mol of proton sponge salt. Observation of a single resonance in the ³¹P NMR and a triplet for OH suggests a symmetrical structure for this cation with two equal Au-O interactions, possibly stabilized by a single aurophilic interaction. Other diaurated oxonium ions $(LAu)_2OH^+$ were obtained also with ligands L = L3 (11), IMes (12), IPr (13) as sole products of reactions of 3, 5, and 6 with proton sponge according to Equation (26a) in Scheme 2. However, DTBPAuOTf (4) reacted with proton sponge to give triaurated oxonium ion $(DTBPAu)_3O^+$ (14) [Scheme 2, Eq. (27)]. Proof of the molecular composition of oxonium ions obtained by these reactions comes not only from the presence or absence of OH protons, but simply from reaction stoichiometry, easily established by integration of relevant peaks in their spectra. $(IPrAu)_2OH^+$ (13) was previously described by Nolan et al. in 2010 and until now was the only known example of diaurated oxonium ions.^[16] According to Nolan et al., the X-ray structure of 13 contained Au-Au interactions somewhat longer than it would be expected for aurophilic interactions. Therefore, it is doubtful whether they contribute to the stability of this type of structures in our case.

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The cation $(L2Au)_2OH^+$ (10) can also be generated with other bases. For example, even 2,6-di-tert-butylpyridine reacts with 2 to give 10, but the reaction is reversible: two equivalents of the base are able to transform only half of the starting complex. Solid LiOH, and even simple water extraction, trigger quantitative formation of 10, but when a solution of 2 in CDCl₃ is treated with 10% aqueous KOH, fast reaction occurs to give L2AuOH 15 as sole product [Scheme 3, Eq. (28)]. Its proton spectrum exhibits a characteristic broad singlet at -0.73 to -0.76 ppm corresponding to the OH proton. The exact chemical shift of the proton is slightly affected by the presence of water, which forms strong hydrogen bonds and causes exchange of the protons, so that no coupling to phosphorus is observable.^[17] Indeed, in an extra-dry solution of 15 in C_6D_6 (above solid KOH) the OH proton could be observed as a doublet at -0.20 ppm (${}^{3}J_{H-P}=4.8$ Hz), and the doublet was also nicely observed in the NMR spectrum of 15 in C₆D₆ layered above saturated aqueous KOH solution.

Complex L2AuOH (15) is an example of a gold hydroxide, a new class of gold complexes. Currently, only a single

$$\begin{array}{c} L2AuNCMe^+ + OH^- & \begin{array}{c} CDCl_3 \\ \hline KOH_{aq} \end{array} & \begin{array}{c} L2AuOH + MeCN \\ 15 \end{array}$$
(28)

 $2 L2AuNCMe^{+} + OH^{-} \longrightarrow (L2Au)_2OH^{+} + MeCN$ (29) 10 $(12Au)_2OH^{+} + OH^{-} = 2 2 I2AuOH$ (20)

$$\begin{array}{c} (L2Au)_{2}OI^{+} + OI^{+} & \longrightarrow \\ 10 & 15 \\ (Au)_{2}OI^{+} + L2AuOH & \longrightarrow \\ (L2Au)_{3}O^{+} + H_{2}O \end{array}$$
(31)

10 15 17

(L2

 $15 + CH_2(CO_2Me)_2 \longrightarrow L2AuCH(CO_2Me)_2 + H_2O$ (32)
(32a) $L2AuOH + CDCI_3 \xrightarrow{PPh_3 (cat.)} L2AuCCI_3 + H_2O$ (33a)
16







Scheme 3. Formation of gold hydroxide and its transformations.

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example is known in the literature. In 2010 Nolan described IPrAuOH and studied the chemistry of this compound, which exhibited strongly basic properties.^[2e,18] In complete accordance with expectations, L2AuOH appeared to be a strong base as well. It readily reacted with dimethyl malonate to give L2AuCH(CO₂Me)₂ [Scheme 3, Eq. (32)]. In CDCl₃ solution L2AuOH slowly reacts with the solvent (over many hours at room temperature), but the reaction can be strongly accelerated by PPh₃ [Scheme 3, Eqs. (33a) and (33b)]. Thus, when a catalytic amount of PPh₃ (≈ 1 -5%) was added to a solution of L2AuOH in CDCl₃ and the solution concentrated in vacuo, the residue already contained only the products of the reaction. Normally, a mixture of L2AuCl and $L2AuCCl_3$ (16) is formed. The chloride ion in L2AuCl must come from CDCl₃ [Scheme 3, Eq. (37)]. We found that the ratio of the products can be controlled by temperature. Thus, when evaporation of the reaction mixture was conducted below room temperature, 16 could be obtained as a main product ($\approx 95\%$), only slightly contaminated with L2AuCl, while formation of L2AuCl is favored at higher temperature. Interestingly, 16 has exactly the same phosphorus chemical shift as 10 and L2AuDMAP+ (57.43 ppm) in CDCl₃ solution, but the proton spectra differ sufficiently to allow differentiation. Unfortunately, a ¹³C spectrum did not prove the presence of the CCl₃ residue. However the structure was unambiguously established by Xray analysis (Scheme 3). The catalytic action of PPh₃ in this reaction is explained by its enhancing dissociation of L2AuOH, to provide OH⁻, which is very reactive in organic solution due to lack of solvation and should deprotonate chloroform more readily [Scheme 3, Eq. (34) and (35)]. Control experiments in C_6D_6 revealed that PPh₃ is unable to stoichiometrically displace OH- from gold (even in excess) and the reaction is thus highly reversible [Scheme 3, Eq. (34)]. Another test performed on 15 with TMTU indicated no sign of any exchange even if TMTU was present in excess. Rather, prolonged warming of the reaction mixture caused hydrolysis of TMTU to give (Me₂N)₂CO and some complexes with sulfur. These results might seem surprising, given the general low oxophilicity of gold, but on the other hand OH⁻ is a highly nucleophilic ion whose elimination from a covalent compound like LAuOH is disfavored in the absence of good OH⁻ acceptors. Obviously, the OH of gold hydroxide has strong desire to interact with more suitable electrophiles, (e.g., with a proton). In other words, LAuOH can be viewed as soluble covalent organic analogue of KOH.

Since gold hydroxides are promising catalyst precursors activated by protonation and useful reagents for the synthesis of various organogold compounds,^[19] we turned our attention towards their improved synthesis. Thus, the previously described example IPrAuOH was synthesized by heating a solution of IPrAuCl in THF/toluene with solid KOH for 24 h, which is a rather long and harsh procedure but nevertheless gave the product in high yield. We were pleased to find that the analogous reaction of *L*2AuCl with solid KOH occurred in less than 1 min at room temperature under mechanical stimulation. Thus, when a benzene solution of the starting gold complex was ground in a small mortar with solid KOH followed by simple filtration through Celite, a solution of about 95% pure product was obtained [Eq. (39)]. We were even more surprised when we found that this reaction occurs within 5 min at room temperature upon shaking a benzene solution of L2AuCl with concentrated aqueous KOH. It appears that OH⁻ can displace Cl⁻ from gold even in solution, which was not previously recognized. In the same way, IPrAuOH and IMesAuOH were prepared as well. However the corresponding chlorides reacted more sluggishly than L2AuCl. Notably, neither of these methods was successful for the preparation of Ph₃PAuOH, whose existence has so far not been confirmed.

LAuCl + KOH_(s)
$$\xrightarrow{C_6D_6}$$
 LAuOH + KCl_(s) (39)
L = *L*2, IMes, IPr

We further studied the chemistry of $(L2Au)_2OH^+$ (10) and L2AuOH (15). When a solution of 10, generated by reaction of 2 with PrSp, was treated with another nucleophile (Nu), quantitative formation of $L2AuNu^+$ occurred [Eq. (40)]. Accordingly, PrSp is completely restored from the salt. This transformation is triggered already by Me₂S, which demonstrates high reactivity of 10 in the presence of a proton donor. In the absence of a proton donor, however, other pathways are followed (see below).

$$(LAu)_2OH^+ + 2Nu + PrSpH^+ \longrightarrow LAuNu^+ + PrSp + H_2O$$
(40)

With regard to chemoselectivity, an interesting subject would be the reaction with simple amines, as they can act both as bases and ligands. To check this possibility, we conducted NMR titration of 2 with triethylamine. An interesting situation occurred before the equivalence point: $L2AuNEt_3^+$, 10, and the remaining 2 were all simultaneously observed, together with the corresponding amount of Et₃NH⁺. Closer to the equivalence point, the amount of $(L2Au)_2OH^+$ (10) and 2 decreased, while $L2AuNEt_3^+$ was formed as the major product. This situation can be described by Equations (41) and (42). Traces of $(L2Au)_2OH^+$ were still detectable in the presence of 1.5 equivalents of Et₃N. This experiment demonstrated that initially some competition took place, but with increasing amount of Et₃N it reacted preferentially as a ligand and not a base.^[20] When TMTU was added to this solution, complete substitution of Et₃N occurred to give the L2AuTMTU⁺ complex. In contrast, Lut, Pic, and DMAP reacted with 2 exclusively as ligands and not as bases, regardless of the molar ratios, as was described above [Figure 2, Eq. (4)].

- $L2AuNCMe^{+} + Et_{3}N \longrightarrow L2AuNEt_{3}^{+} + MeCN$ (41)
- $L2AuNEt_3^+ + L2Au^+ + H_2O \longrightarrow (L2Au)_2OH^+ + Et_3NH^+$ (42)

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Then we titrated a freshly prepared $(Ph_3PAu)_3O^+$ (9)/ PrSpH⁺ mixture with triethylamine and found that gradual formation of Ph₃PAuNEt₃⁺ occurred, but the equilibrium now lay on the left: approximately nine equivalents of Et₃N were able to transform only about 60% of 9 into the triethylamine complex [Eq. (43)]. During this experiment both **9** and $Ph_3PAuNEt_3^+$ were observed clearly by ³¹P NMR. When TMTU was added to the final solution, one broad phosphorus resonance was observed for all the species. This suggests that Et₃N was completely substituted from gold, but then Ph₃PAuTMTU⁺ got involved in a fast exchange process, together with (Ph₃P)₂Au⁺, which was present in solution as impurity from the beginning but was not involved in any fast exchange before TMTU was added. Also, this experiment allowed the stability of the two species (LAu)₃O⁺ and (LAu)₂OH⁺ to be compared. Obviously (LAu)₃O⁺ should be more stable because it is stabilized by three aurophilic interactions, while (LAu)₂OH⁺ has only one, albeit doubtfully. The situation may change with the size of the ligand, and we postulate that this accounts for the relative instability of (LAu)₃O⁺ when a bulky phosphine ligand is present; there is simply not enough space around the oxygen atom for three big fragments, and only formation of less aurated (LAu)₂OH⁺ is possible.

$$(Ph_{3}PAu)_{3}O^{+} + 3 Et_{3}N + 2 PrSpH^{+} \Longrightarrow Ph_{3}PAuNEt_{3}^{+} + 2 PrSp + H_{2}O$$
(43)

Also, we studied conversions of $(L2Au)_2OH^+$ (10) and L2AuOH in both directions in three different solvents $(CDCl_3, CD_2Cl_2, [D_8]THF)$. When PPh₃ was added to a solution of $(L2Au)_2OH^+$, formation of new species was observed, which eventually were converted to L2AuOH when more PPh₃ was added [overall Eq. (44) in Scheme 4]. The same species were detected during the synthesis of L2AuOH, when a solution of 2 in CDCl₃ was shaken briefly with 10% aqueous KOH. On further brief shaking, L2AuOH was cleanly formed, according to Equation (28) in Scheme 3. From these observations, we concluded that these new species adopt the intermediate position between $(L2Au)_2OH^+$ and L2AuOH during the reaction with hydroxide ions. From general Equations (46)–(48) in Scheme 4 it becomes clear that the quantity of hydroxide ions per

$$(L2Au)_2OH^+ + PPh_3 \longrightarrow L2AuOH + L2AuPPh_3^+$$
(44)
10 15

$$(L2Au)_2OH^+ + L2AuOH \longrightarrow (L2Au)_3O^+ + H_2O$$
 (45
10 15 17

$$1 \qquad \begin{array}{c} 1 \\ \downarrow q \\ \checkmark \end{array} \qquad \begin{array}{c} LAu^{+} + OH^{-} \longrightarrow LAuOH \qquad (48) \end{array}$$



mole of gold increases for the following syntheses: $(LAu)_2OH^+ < (LAu)_3O^+ < LAuOH$. Hence, we concluded that the new species intermediately arising and disappearing on the way from $(L2Au)_2OH^+$ (10) to L2AuOH (15) must be $(L2Au)_{3}O^{+}$ (17). We automatically concluded that 10 and 15 react with each other to give $(L2Au)_3O^+$ (17) according to Equation (45) in Scheme 4. This process was found to be reversible, because 17 was often observed in mixture simultaneously with both 10 and 15 and not just with one of them or pure. Accordingly, brief appearance of 17 during the synthesis of L2AuOH by Equation (28) in Scheme3 corresponds to incomplete reaction when a mixture of 10 and 15 arises [Scheme 3, Eqs. (29)-(31)]. However, only in THF was $(L2Au)_3O^+$ observed free of 10 and 15. It remains unclear if this is due to better stability of $(L2Au)_{3}O^{+}$ in this solvent or some kinetic circumstances. Note that $(L2Au)_3O^+$ is not an intermediate on the way from 10 to 15; it is rather a temporary side product. The same is valid when 15 is transformed into 10 by addition of **2**. Formation of $(L2Au)_3O^+$ was rather unexpected given the increased steric bulk of the building blocks, but this ion is stable enough to be detected by ESI MS.

Compound $(L2Au)_2OH^+$ (10) can be viewed as a complex of $L2Au^+$ with L2AuOH as ligand, and thus Equation (44) in Scheme 4 can be viewed as simple ligand exchange. To get an idea how strong L2AuOH is as a ligand, we conducted reactions with weaker nucleophiles in place of PPh₃ and found that this reaction reversibly occurs already with Me₂S, and with lutidine the equilibrium is much shifted to the right.

Thereafter, the analogous interconversion of $(L3Au)_2OH^+$ (11) and L3AuOH (18) was studied [Eq. (49)], but in contrast to the previous case it appears to be a mechanistically "clean" transformation giving no intermediate species. In no situation was the corresponding triaurated oxonium ion $(L3Au)_3O^+$ observed [Eq. (50)]. Possibly, it cannot exist at all given the increased steric hindrance in comparison to $(L2Au)_3O^+$.

$$(L3Au)_{2}OH^{+} + PPh_{3} \longrightarrow L3AuOH + L3AuPPh_{3}^{+}$$
(49)
$$(L3Au)_{2}OH^{+} + L3AuOH \xrightarrow{} (L3Au)_{3}O^{+} + H_{2}O$$
(50)

Finally, we studied reaction of 2 with proton sponge in methanol [Eq. (51)]. In contrast to the previous solvents, no clear situation was observed. Possibly, an equilibrium mixture of several oxonium and methoxonium species was formed. However, when solid KOH was added to this mixture, *L*2AuOMe (19) was generated cleanly. Its identity was established by reaction with PPh₃, giving clean substitution and no other products. Obviously, proton sponge was not strong enough to generate this methoxide.

2
$$\xrightarrow{\text{PrSp}}$$
 unidentified $\xrightarrow{\text{KOH}}$ L2AuOCD₃ $\xrightarrow{\text{PPh}_3}$ L2AuPPh₃⁺ (51)

Chem. Eur. J. 2012, 00, 0-0

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So far no oxonium species have been described for binuclear gold complexes. Therefore, in line with the previous chemistry, we studied reactions of **7** and **8** with proton sponge. As above, by integration it was established that **7** reacts with proton sponge to give triaurated oxonium ions for which the simplest molecular composition was established to be $(dppfAu_2)_3O_2^{2+}$ (**20**) according to Equation (52) in Scheme 5, while **8** gave a kind of diaurated oxonium ion, for

3 dppf(AuOTf)₂ + 4 PrSp + 2 H₂O
$$\longrightarrow$$
 (dppfAu₂)₃O₂²⁺ + 4 PrSpH⁺ + 6OTf⁻
7 20 (52)
S-Tol-BINAP(AuOTf)₂ + PrSp + H₂O \longrightarrow
8 S-Tol-BINAP(Au)₂OH⁺ + PrSpH⁺ + 2 OTf⁻ (53)
21

3 S-Tol-BINAP(Au)₂OH⁺ + LiOH
$$\longrightarrow$$
 (S-Tol-BINAP(Au)₂)₃O₂²⁺ + Li⁺ + H₂O
8 22 (55)



possible structures for $(dppfAu_2)_3O_2{}^{2+}$ ${\color{black}{20}}$ and $(S\text{-Tol-BINAP}(Au)_2)_3O_2{}^{2+}$ ${\color{black}{22}}$



possible structures for S-Tol-BINAP(Au)₂OH⁺ 21

Scheme 5. Reactions of binuclear gold complexes with bases.

which the simplest molecular composition was established as $L8(Au)_2OH^+$ 21, [Scheme 5, Eq. (53)]. In the ¹H NMR spectrum 21 exhibits a characteristic, slightly broad singlet at +5.36 ppm, corresponding to a single OH proton (in relation to 2Au), while in the ³¹P NMR spectrum it shows a single sharp resonance at 22.85 ppm. In comparison with other such species the position of the OH signal is abnormal. On addition of solid LiOH to a solution of 21 a new species is formed, which was tentatively assigned the formula $[L8(Au)_2]_3O_2^{2+}$ (22). This can be directly obtained by reaction of 8 with solid LiOH, its ¹H NMR spectrum exhibits no protons assignable to OH, and its ³¹P NMR spectrum exhibits a single sharp resonance at 21.35 ppm. However, exact structures were not determined for either of these species. Based on the information on structures of known oxonium species, and from the fact that 20, 21, and 22 all exhibit a single phosphorus resonance, symmetric structures are proposed (Scheme 5).



So far we described homoleptic aurated oxonium species and it is of interest to check whether some mixed aurated oxonium complexes, a previously unknown type of compounds, can be observed. For this purpose we studied the reaction of $(L3Au)_2OH^+$ (11) with 2 in the presence of excess proton sponge and found that 11 and 10 exist in equilibrium with the mixed species $(L2Au)(L3Au)OH^+$ (23), and the equilibrium constant was determined to be 0.87 [Scheme 6,

$$(L2Au)_{2}OH^{+} + (L3Au)_{2}OH^{+} \xrightarrow{CDCl_{3}} 2 (L2Au)(L3Au)OH^{+} \quad K_{eq} = 0.87 \quad (56)$$
10
10
11
23
4 (Ph_{3}PAu)_{3}O^{+} + 3 (L2Au)_{2}OH^{+} + PrSp \longrightarrow
9
10
6 (Ph_{3}PAu)_{2}(L2Au)O^{+} + PrSpH^{+} + H_{2}O \quad (57)
24
2 (Ph_{3}PAu)_{2}(L2Au)O^{+} + (L2Au)_{2}OH^{+} + PrSp \longrightarrow
24
4 (Ph_{3}PAu)_{2}(L2Au)O^{+} + (L2Au)_{2}OH^{+} + PrSp \longrightarrow
25
4 (Ph_{3}PAu)_{3}O^{+} + 3 (L3Au)_{2}OH^{+} + PrSp \longrightarrow

9 11 6
$$(Ph_3PAu)_2(L3Au)O^+ + PrSpH^+ + H_2O$$
 (59)
26
24: $L_1 = PPh_3, L_2 = L_2$
25: $L_1 = L_2, L_2 = PPh_3$
26: $L_1 = PPh_2, L_2 = PPh_3$
26: $L_1 = PPh_2, L_2 = PPh_3$

Scheme 6. Formation of mixed oxonium species.

Eq. (56)], .^[21] In the ¹H spectrum **23** exhibits a triplet for the OH proton with a chemical shift (-0.36 ppm) between the corresponding values for the homoleptic species. In the ³¹P NMR spectrum **23** exhibits two singlets in a 1:1 ratio. Further, we conducted titration of $(Ph_3PAu)_3O^+$ (9) with 2 in the presence of excess proton sponge. In the early stage, formation of 10 did not occur at all. Rather, formation of a single product $(Ph_3PAu)_2(L2Au)O^+$ (24) occurred quantitatively until almost all 9 had reacted [Scheme 6, Eq. (57)]. Interestingly, in the ³¹P NMR spectrum this compound exhibits no P-P coupling and gives two singlets in 2:1 ratio. On further addition of 2, the simultaneous formation of two compounds (10 as major and $(Ph_3PAu)(L2Au)_2O^+$ 25 as minor product) indicates a reversible process [Scheme 6, Eq. (58)]. Obviously, formation of $(Ph_3PAu)_2(L2Au)O^+$ (24) with three possible aurophilic interactions is rather favored over formation of 10 in the presence of 9, but this does not hold true for $(Ph_3PAu)(L2Au)_2O^+$ (25). This directly reflects the stability of these species, which decreases as they become more crowded. Thus, in the case of $(L3Au)_2OH^+$ (11) formation of 26 is already highly reversible [Scheme 6, Eq. (59)], while formation of (Ph₃PAu)(L3Au)₂O⁺ was not observed at all. Notably, phosphorus chemical shifts of the ligand residues in these mixed oxonium species are very close (within 0.3 ppm) to those observed in $(Ph_3PAu)_3O^+$ and $(L2Au)_{3}O^{+}$, which demonstrates similarities between all of these compounds. Assuming that the equilibrium [Scheme 6, Eq. (58)] is pH-dependent, we attempted to shift it to the right with KOH, a stronger base. However, the equilibrium did not change significantly: both 24 and 25 were still observed; however, 10 completely transformed into L2AuOH. We suppose that reaction of 10 with KOH to give 15 [Scheme 3, Eq. (30)] simply happened much faster than complex rearrangement by Equation (58) in Scheme 6.

Finally, we titrated $L8(Au)_2OH^+$ (21) with 9 in the presence of proton sponge and found that two new products were formed simultaneously, [Scheme 7, Eqs. (60), (61)].



{(S-Tol-BINAP(Au)₂)(Ph₃PAu)O}₂²⁺

Scheme 7. Formation of mixed oxonium species bearing bidentate ligands.

However, one of them completely transformed into another species when more 9 was added. The molecular composition this intermediate species was established of as $\{(L8(Au)_2)_2OH\}(Ph_3PAu)O^{2+}$ (27) since in the ¹H spectrum it exhibits OH and Me signals in the ratio 1:12:12. The final product did not contain any OH signals, and its simplest molecular composition was established as $\{L8(Au)_2\}$ - $(Ph_3PAu)O^+$ (28) which can be a monomer or dimer. The exact structures of these ions were not determined; possibly, symmetric structures are formed.

The interconversion between different kinds of oxonium ions and gold hydroxide can be explained by a general mechanism outlined in Scheme 8, consisting of principally all reversible steps, so that position of the real system at equilibrium primarily depends on the molar ratio and nature of reactants. Accordingly, reaction between LAu+ and a base might begin with formation of a hydrate I, which would undergo a second addition of LAu⁺ to give tetracoordinate oxonium ion II, which would readily expel one proton to give intermediate (LAu)₂OH⁺ (III). If high OH⁻



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interconversion between LAuOH, (LAu)₂OH, (LAu)₃O⁺ in the presence of OH⁻:

VI



Scheme 8. General mechanism of formation and transformation of oxonium species and gold hydroxide.

concentration is provided from the beginning, direct substitution at gold might take place as ordinary ligand exchange. Further, **III** reacts with LAu⁺ to finally give oxonium ion **V** via tetracoordinate oxonium ion IV or, alternatively, III reacts with OH⁻ to give two equivalents of LAuOH. This process can be viewed as a simple ligand exchange at gold, if one considers III as a complex of LAu⁺ with LAuOH as a ligand. Correspondingly, it is easy to trace the process back when acid is added to LAuOH or V. The intermediacy of tetracoordinate oxonium species like II and IV is postulated, but gains support from the ability of V to form isolable tetracoordinate oxonium ion VI, which has been known since 1995.^[22] Obviously, despite the cationic character of III and V, the oxygen atom still can act as a nucleophile, providing its fourth electronic pair to a proton or gold. The relative nucleophilic nature of oxygen in these species becomes clearer if one considers electronic density distribution within a molecule. Indeed, according to the concept of hard and soft Lewis acids and bases, there should be relatively weak interaction between Au and O, with little positive charge transfer from gold to oxygen. It can be argued that the oxygen atom in V is more electron rich than that in III and far more electron rich than that in H_3O^+ , despite the fact that gold is more electronegative than hydrogen. This hy-

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pothesis gains further support from NMR spectra, which typically show chemical shift of OH in **III** below 0 ppm. The same statements can be made to account for the strongly basic properties of LAuOH.

However, to account for reversible formation of V during transformation of (LAu)₂OH⁺ into LAuOH under basic conditions, equilibria V=IV=III are not feasible, due to the absence of H⁺. In this case we propose alternative mechanisms, which are also given in Scheme 8. Thus, one might consider direct reaction of V with water, through hydrogen-bond activation, to give an equilibrium mixture of III and LAuOH. From here, transformation of III to LAuOH in the presence of OH- is clear. Alternatively, one can consider the possibility of V reacting directly with OH⁻, but then formation of gold oxide VIII would follow. However, at present, such gold derivatives remain unknown and their intermediacy is thus highly speculative. But if formed, they would be highly basic substances and would react immediately with water to give initially III and OH⁻ and finally lead to LAuOH. We conclude that, depending on the availability of H⁺ and OH⁻, gold may undergo transformations in different directions through different pathways, but the final outcome of a reaction would be dependent on the molar ratio and nature of reactants.

Formal LAu⁺ exchange at oxygen between $(LAu)_3O^+$ and $(L'Au)_3O^+$ was previously observed, but nothing was said about formation of any mixed intermediate species on the way.^[23] In our study, due to the presence of at least one large unit, such exchanges were observed as stepwise processes for the first time.

Reaction of 2 with Li₂S: complexes with sulfur and their interconversion: When 2 was allowed to react with substoichiometric amounts of Li2S in a biphasic CDCl3/H2O mixture, $(L2Au)_3S^+$ (29) was formed as a sole product [Eq. (62)]. Under these reaction conditions formation of tetraaurated sulfonium ion $(L2Au)_4S^{2+}$ could be expected, and exclusive formation of 29 evidences for inability of any higher coordinated compound to exist due to steric reasons.^[24] On further addition of excess Li₂S, multiple processes occurred. Thus, 29 predominantly transformed into hydrosulfide L2AuSH (30), but the reaction was also accompanied by formation of several minor products [Eqs. (63) and (64)]. Among them, free ligand L2 was identified. Liberation of free L2 implies that part of the gold was converted to Au₂S, and this idea gains support from the fact that some brown precipitate was indeed observed. The same decomposition was described in the case of (Ph₃PAu)₂S long ago,^[25] and later the structure of this compound could be established by X-ray analysis.^[26] Accordingly, we concluded that neutral sulfide (L2Au)₂S would also be unstable: it either decomposes to Au₂S and L2 or is hydrolyzed back to hydrosulfide 30. Notably, complete precipitation of Au₂S and liberation of L2 could not be achieved, at least within a short time interval. The structure of $(L2Au)_3S^+$ was established by X-ray analysis (Scheme 9). The ligand residues are located in such a way that the cation can be described as having



 $(L2Au)_2SH^+ + L2AuSH \longrightarrow (L2Au)_3S^+ + H_2S$ (67) 29

 $2 L2AuSH + L2Au^{+} \longrightarrow (L2Au)_{3}S^{+} + H_{2}S$ 30 2 29(68)

$$\begin{array}{cccc} (L2Au)_{3}S^{*} + H_{2}S + L2Au^{*} & \longrightarrow & 2 & (L2Au)_{2}SH^{*} & (69) \\ \hline 29 & 2 & 31 \\ (L2Au)_{2}SH^{*} + L2Au^{*} & \longleftarrow & (L2Au)_{3}S^{*} + H^{*} & (70) \end{array}$$



Scheme 9. Formation and transformations of complexes with sulfur.

a C_3 symmetry axis passing through the central sulfur atom and perpendicular to the base of the Au₃S pyramid.

 $3 L2Au^{+} + Li_2S_{(aq)} \xrightarrow{CDCI_3/H_2O} (L2Au)_3S^{+} + 2 Li^{+}_{(aq)}$ (62)

$$(L2Au)_{3}S^{*} \xrightarrow{CDCI_{3}} L2AuSH + (L2, and other unidentified products) (L2, and other unidentified products) (63)$$

$$(L2Au)_{3}S^{+} + 2 S^{2-} + 3 H_{2}O \longrightarrow 3 L2AuSH + 3 OH^{-}$$
 (64)
29 30

Interestingly, when a chloroform solution of **2** was ground in a mortar together with excess of solid Li₂S (even without addition of water), clean formation of L2AuSH (**30**) occurred and no brown Au₂S color or free L2 was observed, [Scheme 9, Eq. (65)]. Based on this fact, we suppose that **30** is the only stable ultimate product of the reaction with sulfide (correspondingly, formation of LiOH should be invoked to account for this process). In the ¹H NMR spectrum **30** exhibits a characteristic doublet at -1.44 ppm corresponding to a single SH proton.

Transformations of L2AuSH (30) were further studied in the following experiment. When 2 was added to a fresh solution of 30 in CDCl₃, $(L2Au)_3S^+$ (29) was formed as sole product [Scheme 9, Eq. (68)]. This reaction is accompanied by liberation of H₂S, which could be also recognized by smell. On further addition of 2, 29, H₂S, and 2 reacted to give $(L2Au)_2SH^+$ 31 as sole product, [Scheme 9, Eq. (69)].

In the ¹H NMR spectrum it exhibited a characteristic triplet at -0.41 ppm (${}^{3}J_{H-P} = 5.3$ Hz), corresponding to a single SH proton. Ultimately, when more 2 was added, 29 reappeared again, but now reversibly [Scheme 9, Eq. (70)]. These interesting transformations are explained as follows. Initially, when L2AuSH reacts with 2, $(L2Au)_2SH^+$ would be expected as a direct product [Scheme 9, Eq. (66)]. Observation of **29** at an early stage implies that $(L2Au)_2SH^+$ quantitatively reacted with 29 to give $(L2Au)_3S^+$ and H_2S [Scheme 9, Eq. (67)], and only when no more 30 is present in solution is further reaction possible. Next, when (L2Au)₂SH⁺ reacted with an excess of 2, formation of $(L2Au)_3S^+$ occurred, but now liberation of super acid HSbF₆ makes this process reversible. However, the equilibrium could be completely shifted to the right on extraction with water. Such an interesting appearance, disappearance, and reappearance of $(L2Au)_{3}S^{+}$ 29 is completely understandable if one considers material balance in the system. Thus, the initial formation of 29 happens before one equivalent of gold is added according to Equation (68) in Scheme 9. At this moment the molar ratio of elements in the system is $Au^{+}/S^{2-}/H^{+}=3/2/2$ (1S) and 2H are present as H₂S and unreactive). Stoichiometric formation of 31 happens exactly when the molar ratio is $Au^+/S^{2-}/H^+ = 2/1/1$, as in the compound. Finally, 29 reappears again when Au/S>2/1 and becomes complete provided Au⁺/S²⁻=3/1 and no acid is present.

From these two experiments it can be concluded that the outcome of the reaction between 2 and S^{2-} depends on the molar ratio of reactants and availability of reactive protons. The mechanism of these transformations would resemble the previously described mechanism for oxonium species.

An attempt was made to synthesize the elusive neutral $(L2Au)_2S$ by reaction of 30 and 15 in C_6D_6 , but this led to mixtures of products. Interestingly, liberation of free L2 was observed, but now it was not accompanied by any brown precipitate, which suggests that formation of colorless products of general formula $(L2Au)_2$ S·x Au₂S could be possible. Four new components were observed in the NMR spectra of these mixtures; two of the compounds contained characteristic singlets at -0.61 and -0.66 ppm (in C₆D₆); none of them was identified. One of the products precipitated from benzene. The solid was soluble in chloroform and did not exhibit any signals below 0 ppm. The crystals, however, were not analyzed by X-ray analysis leaving this puzzle to be solved in the future.

Conclusion

We have thoroughly investigated the coordination chemistry of modern gold catalysts by NMR spectroscopy in solution. This included simple ligand-exchange reactions at gold, as well as formation and transformations of different oxonium and sulfonium species. Success in this study relied on the presence of bulky ligands in gold complexes, which allowed the transformations to be traced by NMR clearly without being spoiled by the dynamic situations that often happen

with complexes bearing small ligands. By observation of discrete rather than continuous changes in NMR spectra, we were able to detect and characterize intermediates and got closer insight to mechanisms of processes involving multiple reactive species.

Experimental Section

Synthesis of 2: An improved literature procedure was used.^[27] AgSbF₆ (0.213 g, 0.620 mmol) was quickly weighed in a vial. To this was added cold MeCN ($\approx 0.3 \text{ mL}$) and CH₂Cl₂ (0.3 mL) to make a clear solution (dissolution of AgSbF₆ in MeCN is rather exothermic). To this solution was added a solution of L2AuCl (0.329 g, 0.620 mmol) in CH₂Cl₂ (3 mL). A white precipitate immediately formed. The reaction mixture was allowed to stand in the dark for about 15 min (rather than overnight as is often given in the literature) before it was passed through Celite (we recommend conducting halogen abstraction reactions by silver in CH2Cl2 as a main co-solvent; see our remarks on synthesis of LAuOTf in the Supporting Information). The reaction flask and filter cake were washed with copious CH2Cl2. The clear colorless filtrate was evaporated in vacuo till dryness and redissolved in a minimum amount of MeCN (≈0.2 mL). This solution was layered with benzene (\approx 1.5 mL) to allow for slow crystallization. First crystals appeared rather slowly, but then crystal growth occurred faster and rather big crystals were obtained. The supernatant was removed by Pasteur pipette and the crystals washed once with benzene and dried in vacuo to yield 2 in about 95% yield. We note that both commercial and self-made 2 normally contain only 0.93 equiv MeCN rather than 1 equiv, and some 10 (\approx 3%) as impurity or as hydrolysis product. However, when the final product was moistened with MeCN and dried in vacuo immediately, but not strongly at first, and then mixed with pentane and finally dried thoroughly, it was possible to obtain the product with 1 equiv MeCN as in the formula.

Synthesis of dppf(AuCl)₂ (7): Solid dppf (0.170 g, 1 equiv) was added to a suspension of Me₂SAuCl (0.101 g, 0.343 mmol, 2.02 equiv) in CH₂Cl₂ (2 mL). All insoluble material soon dissolved to give an almost clear orange solution containing trace amounts of a tiny dark precipitate. The solution was filtered through Celite into a 10 mL flask and additional amounts of CH2Cl2 were used to quantitatively transfer all of the material. The filtrate was concentrated in vacuo to about 0.5 mL. At this point a major part of dppf(AuCl)₂ may already precipitate from the solution. The filtrate was triturated with MeOH to enhance precipitation of the product. The supernatant solution was carefully sucked out (by a Pasteur pipette with a piece of cotton at the end) and the residue washed once with MeOH and dried in vacuo (all in the same flask) to give the desired complex as orange microcrystalline solid in quantitative yield (0.173 g). Note: Me₂SAuCl, dppf and dppf(AuCl)₂ are all practically insoluble in MeOH; therefore it is not recommended to keep more significant deviations from 2/1 molar ratio of the reactants.

S-TolBINAP(AuCl)₂ 8 was synthesized by the same method in quantitative yield. It is also insoluble in MeOH.

Synthesis of (Ph₃PAu)₃O⁺ OTf⁻ (9): A solution of Ph₃PAuCl (171.3 mg, 0.345 mmol) in THF (2 mL) was added to a solution of AgOTf (89.2 mg, 0.347 mmol) in THF (2 mL). AgCl immediately precipitated. The reaction mixture was kept in the dark for 5 min and filtered through a pad of Celite. To the clear colorless filtrate was added a solution of NaOH (15 mg) in water (0.4 mL) and the emulsion was shaken briefly. The product formed as a gray precipitate. The resulting suspension was evaporated almost till dryness. The residue was taken up in CH2Cl2 and water. Any remaining precipitate was filtered off and washed with portions of CH2Cl2. The clear biphasic filtrate was collected, the water phase separated, and the organic phase dried with Na2SO4. After filtration, the clear filtrate was transferred to a weighed round-bottomed flask. Most of the solvent was removed in vacuo and the residue diluted with THF to cause spontaneous precipitation of the pure product as white crystals. The supernatant solution was decanted by Pasteur pipette and the precipitate

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washed with THF once, decanted, and the product dried in vacuo to yield 0.166 g (93%) of the title compound. *Note:* Clearly, the synthesis would be better performed in CH_2Cl_2 solution (change of the solvent from THF to CH_2Cl_2 would be not necessary).

Synthesis of gold hydroxides LAuOH (L=L2, IMes, IPr), mechanochemical method: A suspension of L2AuCl (33.8 mg, 43.8 µmol) and KOH (23.5 mg, 420 µmol, 9.6 equiv) in C_6D_6 (0.5 mL) was ground in a small mortar for 30–60 s (10 s is enough for smaller loadings, and less KOH can also be used). On filtration through Celite (prewashed with C_6D_6) a clear solution of **15** was obtained, which was used directly without isolation. IPrAuCl reacted more slowly, but complete conversion was reliably achieved. Surprisingly, IMesAuCl reacted even more slowly, and complete conversion was not achieved. However, the reaction was clean, and this suggests that prolonged reaction time should achieve complete conversion. We suppose that solubility of the initial and final gold complexes in benzene would be important. We found that L2AuCl and L2AuOH are quite soluble, while IPrAuCl and IMesAuCl are less soluble.

Extractive variant: A solution of LAuCl in CH_2Cl_2 /benzene (1/5) was shaken with concentrated (but not saturated) aqueous KOH for 5 min. The small amount of CH_2Cl_2 was used to improve the solubility of IPrAuCl and IMesAuCl. In principal, pure CH_2Cl_2 can be used, but the efficacy of emulsion generation on shaking and determination of phase separation is lower, while benzene is much better suited. No phase-transfer catalysts are required. Again, reaction of IMesAuCl was found to be rather sluggish. We recommend the mechanochemical method as the simplest and most reliable for synthesis of **15**, while for larger scale synthesis of IPrAuOH some adaptation would be required due to lower solubility in benzene. More remarks on these two procedures are given in the Supporting Information.

Generation of oxonium species (LAu)₂OH⁺ (10-13); comparison of different reagents: Of all bases used in this study only proton sponge generated this species essentially in 100% yield according to Equation (26a) in Scheme 2 regardless of the excess of base. In case of water extraction of a chloroform solution of 2, reaction naturally does not reach completion, but was at least 95% complete (trace amounts of unconverted 2 always remained, as evidenced by the MeCN resonance not exactly at 2.00 ppm and broadening of the OH triplet). When a chloroform solution of 2 was extracted with dilute NaHCO3 solution, the resulting solution contained traces of products of reaction beyond 10, that is, 15 and 17 (as evidenced by the MeCN resonance exactly at 2.00 ppm and broadening of the OH triplet). The use of solid inorganic bases such as LiOH or KOH gave different results depending on the amount of base, particle size, and reaction time. Thus, on brief shaking of a chloroform solution of 2 with relatively coarse LiOH powder, 10 was observed cleanly (at least 95%), while on shaking with bigger amounts of finer powder reaction occurred till exclusive formation of 15. Despite these ambiguities, shaking of a solution of 10 generated by reaction of 2 and PrSp according to Equation (26a) in Scheme 2 with LiOH powder was reliably used several times to get rid of PrSpH⁺ while not disturbing 10.

Acknowledgements

We thank Dr. K. Eichele (Univ. Tübingen, Institut für Anorganische Chemie) and P. Schuler (Univ. Tübingen, Institut für Organische Chemie) for allowing us to use additional NMR spectrometers and Dr. D. Wistuba for HRMS analysis. 120, 2208-2211; Angew. Chem. Int. Ed. 2008, 47, 2178-2181; h) D. J.
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Received: April 10, 2012 Revised: July 30, 2012 Published online:

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Coordination Chemistry of Gold Catalysts in Solution: A Detailed NMR Study



Diving in a gold solution: A detailed exploration of the coordination chemistry of eight gold catalysts by NMR spectroscopy in solution was conducted. This covered ligand-exchange reactions, formation and transformation of different oxonium salts, and complexes with sulfide.