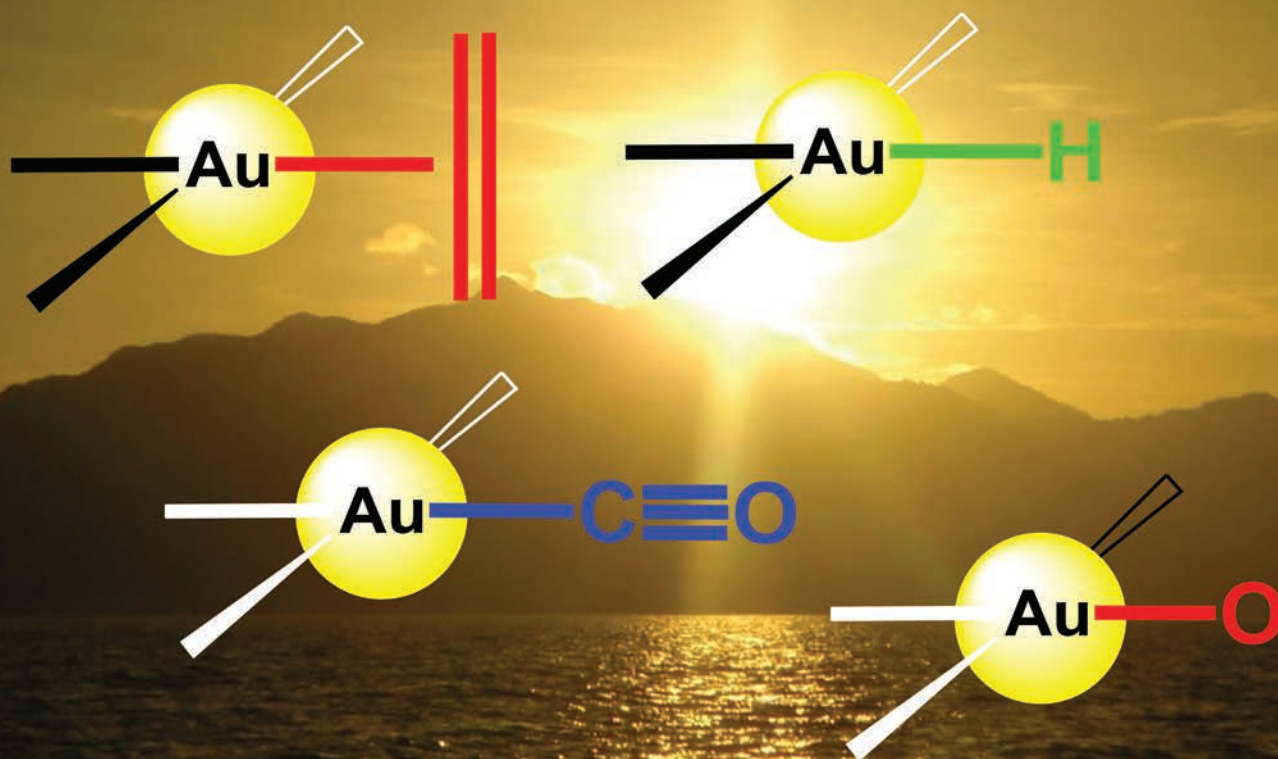


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PERSPECTIVE

Manfred Bochmann *et al.*

An element through the looking glass: exploring the Au–C, Au–H and Au–O energy landscape



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An element through the looking glass: exploring the Au–C, Au–H and Au–O energy landscape

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Gold, the archetypal “noble metal”, used to be considered of little interest in catalysis. It is now clear that this was a misconception, and a multitude of gold-catalysed transformations has been reported. However, one consequence of the long-held view of gold as inert metal is that its organometallic chemistry contains many “unknowns”, and catalytic cycles devised to explain gold’s reactivity draw largely on analogies with other transition metals. How realistic are such mechanistic assumptions? In the last few years a number of key compound classes have been discovered that can provide some answers. This Perspective attempts to summarise these developments, with particular emphasis on recently discovered gold(III) complexes with bonds to hydrogen, oxygen, alkenes and CO ligands.

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Introduction

Gold catalysts, both homogeneous and heterogeneous, have seen a meteoric rise in importance in the last three decades, and interest continues unabated.¹ This has been

amply documented, for example, in special editions of major review journals.^{2,3} For organic transformations, gold in the oxidation state +I is overwhelmingly used as the catalyst, as documented in recent reviews concerning synthetic applications.^{4–8} Important aspects in homogeneous gold(I) catalysis include, *inter alia*, the role of oxidation states, silver activators, ligand structure and the role of counter-anions,⁴ the formation of heterocycles,^{9,10} the nature of gold carbene intermediates,¹¹ the influence of aurophilic interactions¹² on Au(I) catalysis,¹³ silver-free gold catalysts,¹⁴ as

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Joseph Wright obtained his PhD degree from the University of Cambridge in 2003 working on the mechanism of the Wacker reaction under the supervision of Dr Jonathan Spencer. He then undertook postdoctoral positions at the University of Southampton (2003–2004 in the group of Dr Andreas Danopoulos) and at UEA (2005–2008 with Professor Manfred Bochmann and 2008–2012 with Professor Christopher Pickett). In 2012 he was

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well as the important role of counterions and their effect on chemo- and regioselectivity¹⁵ and of chiral Brønsted acids¹⁶ in gold catalysis. Gold(III) catalysts have also found widespread applications in synthetic methodology, most commonly in the form of simple gold salts such as AuCl₃ as catalysts or catalyst precursors.^{17,18} While such catalysts can be fast and efficient, as Schmidbaur pointed out in a recent review,¹⁸ the nature and oxidation state of the catalyst is in most cases difficult to determine and remains a matter of conjecture.

Gold occupies a unique position in the Periodic Table. It is the most electronegative metallic element, with a Pauling electronegativity value close to that of carbon and hydrogen (Au: 2.54; C: 2.55; H: 2.20). As gold(I), with d¹⁰ configuration, it is akin to a main group element, while as gold(III) it behaves as a transition metal and displays a coordination chemistry which mirrors that of other heavy-metal d⁸ ions. The 3rd row elements platinum, gold and mercury are strongly affected by relativistic effects,¹⁹ which cause an expansion of the 5d orbitals and a contraction of the 6s shell and reach their maximum for gold. There are certainly many chemical and structural similarities between the d⁸ systems platinum(II) and gold(III), which have led to platinum and gold catalysts often being compared side-by-side.^{20,21} Numerous reaction mechanisms and intermediates proposed for gold catalysed reactions have been drawn up in analogy to organometallic palladium or platinum catalysts.

However, there are also significant differences between those two neighbours in the Periodic Table. Most prominent are the redox potentials, which are very much more positive for gold than for platinum (values under standard conditions, 1 M aqueous acid, 25 °C):

$$\text{Au}^{3+}/\text{Au}^0 \quad 1.52 \text{ V}$$

$$\text{Au}^{3+}/\text{Au}^+ \quad 1.36 \text{ V}$$

$$\text{Au}^+/\text{Au}^0 \quad 1.83 \text{ V}$$

$$\text{Pt}^{2+}/\text{Pt}^0 \quad 1.19 \text{ V}$$

Gold(III) is therefore very much more readily reduced than platinum(II), to either Au(I) or Au(0), and the formation of purple gold nanoparticles during the course of unsuccessful reactions is only too familiar to practitioners of gold chemistry. The redox chemistry of gold is illustrated, for example, by the ability of “naked” solvated Au⁺ ions to oxidatively cleave benzylic C–H bonds of arenes with an oxidation potential of up to 1.82 V, and even the C–C bonds of diaryl-methanes, to give carbocation intermediates, with metallic gold being generated in the process.²² Oxidation catalysts based on mixtures of AuCl and the diketiminate anion [HC(MeC=NC₆H₃Prⁱ₂)₂][−] have been reported,²³ the assumption being that under such conditions Au(I) diketiminato chelate complexes are generated *in situ* as catalytically active species.²⁴ However, it was shown subsequently that even at 0 °C Au(I) and [HC(MeC=NAr)₂][−] anions lead to the immediate reduction to metallic gold,²⁵ which would seem to suggest that the observed oxidation catalysis is in all probability effected by gold nanoparticles. In other organic transformations, reduction of Au(III) vinyl intermediates to Au(I) could be demonstrated, while the formation of gold nanoparticles could be excluded by X-ray absorption spectroscopy (XAS) methods.²⁶ On the other hand, there are also notable cases where Au(III) vinyl reaction intermediates of the type [(vinyl)AlCl₃][−] and [(vinyl)₂AuCl₂][−], could be isolated and structurally characterised.²⁷

The particular bonding and redox characteristics of gold are of course reflected in the reactivity of the types of intermediates that, by analogy to other metal-catalysed reactions, are assumed to be involved in catalysis: complexes with alkenes and alkynes, CO, metal hydrides and alkyls are all quite reasonable proposals, but, in the case of gold, how much is really known about such compounds? For which ligands or ligand combinations, and for which gold oxidation states, is it realistic to assume the existence, or indeed non-existence, of such species?

Gold, as the embodiment of a noble metal, had long been regarded as unreactive and chemically uninteresting; it is therefore a late-comer to catalysis. This means that many aspects of fundamental organometallic chemistry, which after all forms the basis of our understanding of catalytic mechanisms, remained unexplored for gold. The most dramatic example of this are olefin complexes: whereas platinum(II) provided the first alkene complex of any transition metal, Zeise's salt K[PtCl₃(η²-C₂H₄)], reported in 1827,^{28,29} ethylene

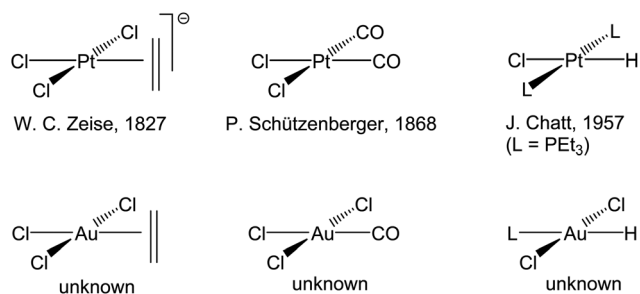


Manfred Bochmann

Manfred Bochmann received his Diploma degree from the University of Marburg in 1977, followed by a PhD at Imperial College London in 1979 with Professor Sir Geoffrey Wilkinson. He worked in ICI central research 1980–83 before moving to a lectureship in inorganic chemistry at the University of East Anglia. He was promoted to a personal chair in 1994. From 1995–2000 he worked at the University of Leeds as Head of In-

organic and Structural Chemistry. On his return to UEA he served as Head of the School of Chemical Sciences and Pharmacy 2006–9 and as Head of the School of Chemistry until 2011. He was awarded the RSC Medal for Organometallic Chemistry in 2003, a Leverhulme Senior Research fellowship in 2011 and an ERC Advanced Grant in 2014. He has published over 280 research articles, several books and numerous patents, mainly on Group 4 metallocene-based olefin polymerisation catalysts. In the last few years his research has concentrated on the organometallic chemistry of gold.





Scheme 1 Classical platinum(II) complex types and their hypothetical gold(III) analogues.

complexes of the isoelectronic Au(III) ion are conspicuous by their absence (Scheme 1). Similarly, hydride complexes of platinum(II) have been known for over 50 years,³⁰ whereas those of Au(III) remained unknown.

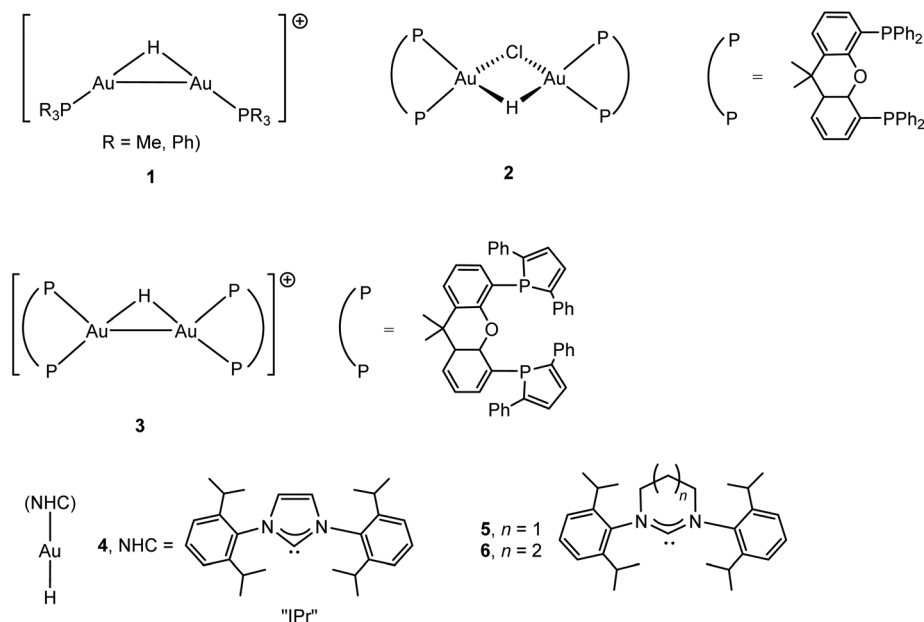
This brief Perspective presents some recent results on the identification and characteristics of some key types of catalysis-relevant gold complexes and tries to highlight the similarities and differences in bonding and reactivity of species with Au–C, Au–H and Au–O bonds. As will be seen, in some cases these gold complexes display a reactivity pattern that is rather different from that of most other transition metal compounds.

The Au–H bond

The chemistry of gold hydrides and compounds with hydrogen bonds to gold have recently been the subject of a comprehensive

review.³¹ Early attempts to generate gold hydride complexes and to stabilise gold(III) with complex anions like BH_4^- and AlH_4^- at -120°C were reported by Wiberg; the result in all cases was reduction to metallic gold.³² The formation of gold hydrides and their stability is of course particularly interesting in connection with catalytic cycles since H-transfer, β -H elimination or M–C bond hydrogenolysis are common reaction steps in transition metal catalysis. The first examples of isolable gold hydrido species were binuclear metal complexes $(\text{CO})_5\text{M}(\mu\text{-H})\text{AuPPh}_3$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $\text{LAu}(\mu\text{-H})\text{ML}_n$ [$\text{ML}_n = \text{IrH}_2(\text{PPh}_3)_3$ or $\text{Pt}(\text{C}_6\text{Cl}_5)(\text{PEt}_3)_2$];^{33,34} all these bimetallic compounds show strongly shielded hydride NMR resonances between $\delta -2$ and -6 ppm (in contrast to terminal $\text{Au}^{\text{I}}\text{-H}$, *vide infra*). Hydrides of gold in oxidation states I, II and III could be identified by vibrational spectroscopy in the reactions of laser-ablated gold atoms condensed into frozen gas matrices at 5 K or below, including $(\text{H}_2)\text{AuH}$, $(\text{H}_2)\text{AuH}_3$, AuH_2 , AuH_4^- and AuH_2^- .³⁵ Evidence for more thermally stable hydride complexes was provided by mass spectrometry, to give ions of type **1**,³⁶ and by NMR studies of the reactions of $(\text{P}^*\text{P})\text{AuCl}$ with PhMe_2SiH , which gave binuclear H-bridged compounds **2** and **3** (Scheme 2); such hydrides are thought to be involved in gold-catalysed alcohol dehydrosilylation. The ^1H NMR hydride signal of **2** was found at $\delta 8.29$ ($J_{\text{PH}} 49.5$ Hz), and while the ^1H signal of **3** could not be detected, the ^2H resonance occurs at $\delta 7.0$ ppm ($J_{\text{PD}} 8.4$ Hz).^{37,38}

The first example of a mononuclear gold(I) hydride was isolated by Sadighi in 2008, $(\text{IPr})\text{AuH}$ (**4**), either by the reaction of $(\text{IPr})\text{AuCl}$ with LiHBEt_3 , or by treating $(\text{IPr})\text{AuO}^t\text{Bu}$ with $\text{HSi}(\text{OMe})_3$ ($\text{IPr} = 1,3\text{-bis}(2,6\text{-diisopropylphenyl})\text{imidazole-2-ylidene}$). The hydride ligand gives rise to a signal with positive chemical shift, at $\delta 5.11$ in C_6D_6 ($\delta 3.38$ in



Scheme 2 Types of gold(I) hydride complexes.



CD_2Cl_2), with an Au–H IR stretching frequency of 1976 cm^{-1} ($\nu_{\text{Au-D}} 1407\text{ cm}^{-1}$).³⁹ The same compound was also made from $(\text{IPr})\text{AuOH}$.⁴⁰ This family of gold hydrides stabilised by N-heterocyclic carbene (NHC) ligands was recently increased by ring-expanded carbenes to give **5** and **6** ($\delta\text{ }^1\text{H}$ 3.57 and 3.15, respectively, in C_6D_6) (Scheme 2). Protonation of **5** or **6** with $[\text{H}(\text{OEt}_2)[\text{B}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4]$ at $-80\text{ }^\circ\text{C}$ gave $\mu\text{-H}$ cations of type **1**, indicated by a high-field shift of the hydride ^1H NMR signal by 4–5 ppm; the suspected intermediate gold dihydrogen complexes $[(\text{NHC})\text{Au}(\text{H}_2)]^+$ could not be detected.⁴¹

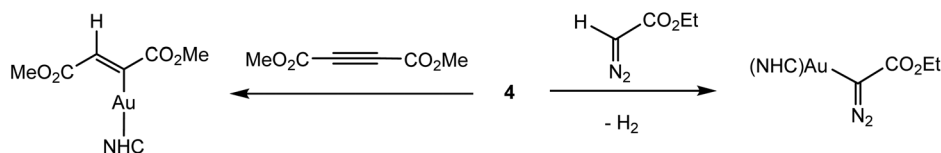
Given the very similar electronegativities of gold and hydrogen, the Au–H bond can be expected to show little “hydridic” character. And indeed, solid **4** is stable to air and moisture at ambient conditions, does not react with protic solvents like *t*-butanol, and reacts only very slowly with benzoic acid. It also does not react with 3-hexyne or diphenylacetylene. On the other hand, dimethyl acetylenedicarboxylate gives a *trans*-insertion product, and ethyldiazoacetate reacts under C–H activation (Scheme 3). The hydride ligand in **4** can however be abstracted by CPh_3^+ to give a binuclear hydride-bridged cation of type **1**, indicated by the high-field shift of the ^1H NMR signal to $\delta 0.42$.³⁹

The mesityl-substituted analogue of **4**, $(\text{IMes})\text{AuH}$, shows low reactivity in the hydrodefluorination of perfluoroarenes, but the reaction is accelerated by *p*-dimethylaminopyridine

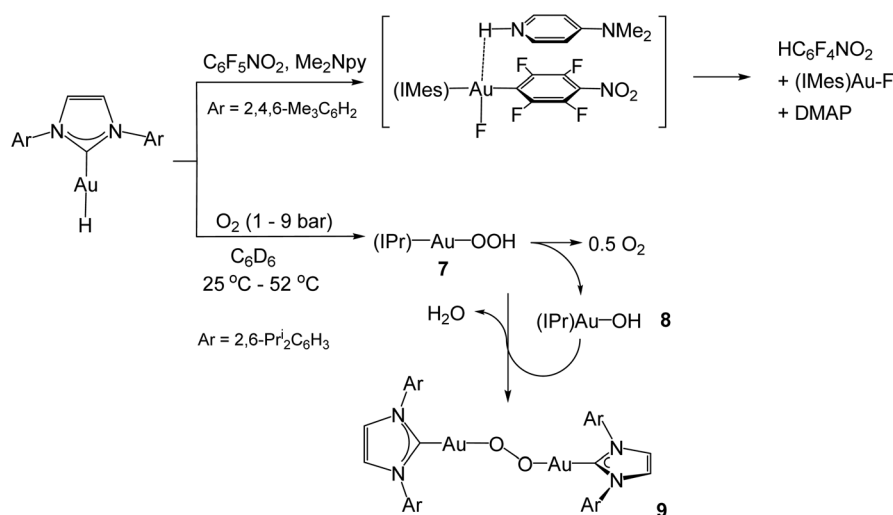
(DMAP) and involves a spectroscopically detectable π -stacked intermediate (Scheme 4).⁴² Under 1–9 bar O_2 , complex **4** undergoes slow dioxygen insertion into the Au–H bond to give the hydroperoxide **7**. The reaction is 1st order in both $[\text{O}_2]$ and $[\text{Au}]$. Product **7** readily decomposes to $(\text{IPr})\text{AuOH}$ (**8**), followed by condensation of **7** with **8** to give the structurally characterised peroxide **9** (Scheme 4).⁴³

The reaction of **4** with stable radicals was used to estimate the Au–H bond energy. Whereas **4** does not react with TEMPO (= 2,2,6,6-tetramethyl-1-piperidyl-*N*-oxide), the hydride ligand is abstracted by galvinoxyl, with formation of the crystallographically characterised galvinoxide salt **10** (Scheme 5). Since the O–H bond dissociation energies (BDEs) of TEMPOH and galvinoxyl-H are 291 kJ mol^{-1} and 329 kJ mol^{-1} , respectively, this provides an estimate of the Au–H bond energy between these two values.⁴³

Gold(I) hydrides could, in principle, also be formed by $\beta\text{-H}$ elimination of gold(I) alkyls, and conversely, the hydrogenation of unsaturated substrates is usually thought of as involving the β -insertion of a coordinated alkene or alkyne into a metal–H bond. Gold(I) is of course a d^{10} system, without suitable energetically accessible vacant orbitals for interacting with a $\beta\text{-C-H}$ bond, nor for the coordination of an olefinic substrate. It is therefore consistent that for $(\text{IPr})\text{AuEt}$ a high barrier for $\beta\text{-H}$ elimination was found, such that this pathway becomes kinetically competitive only above the decomposition temperature of

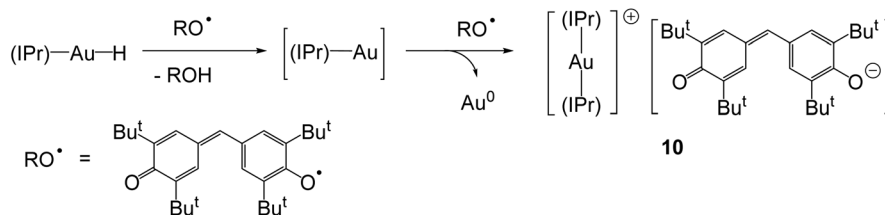


Scheme 3 Reactions of $(\text{IPr})\text{AuH}$.



Scheme 4





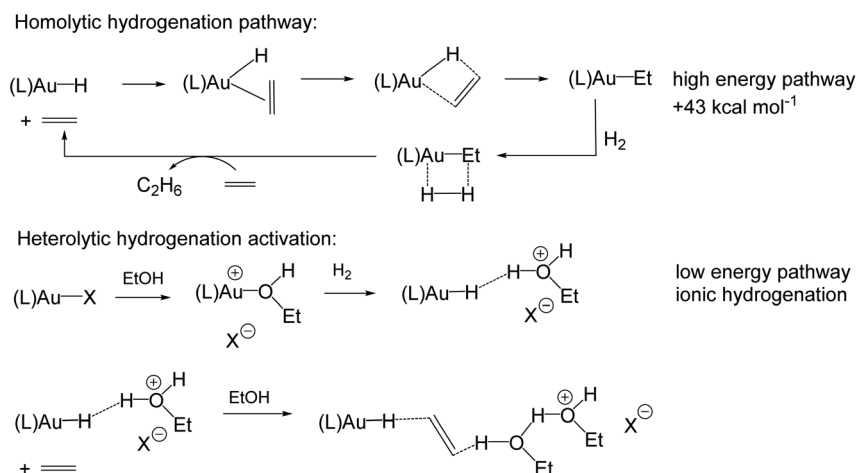
Scheme 5

the complex ($>200\text{ }^{\circ}\text{C}$).⁴⁴ As Bertrand has shown, both β -H and, much more slowly, α -H abstractions from gold alkyls are possible, but only by using an external electrophile such as CPh_3^+ , not however by intramolecular H-transfer reactions.⁴⁵ In line with this, calculations have suggested that for alkene hydrogenations with homogeneous gold(I) catalysts in polar solvents like ethanol, a heterolytic, solvent-assisted H_2 activation pathway prevails over a σ -bond metathesis-type Au-C bond cleavage by an H_2 molecule (Scheme 6). Alkene hydrogenation is thought to follow an ionic mechanism, in which a proton is delivered from the solvent to the alkene. The rate of alkene hydrogenation increases therefore as the stability of the resulting carbocation increases, *e.g.* cyclohexene $>$ ethene. The hydride is delivered from the gold species. Whatever the detailed energetics of these solvent-assisted mechanisms, it is clear that for gold catalysts the ionic reaction profiles are always energetically favoured over the homolytic pathway.⁴⁶

In addition to gold(I) catalysts, gold(III) catalyst precursors are also frequently employed in organic transformations. However, in the large majority of cases the fate of the gold species, the oxidation state and the coordination environment of the resulting gold species under such conditions are a matter of conjecture. The facile reduction of Au(III) to Au(I) suggests that the active species formed *in situ* are most probably gold(I), particularly if catalysts with labile ligands are

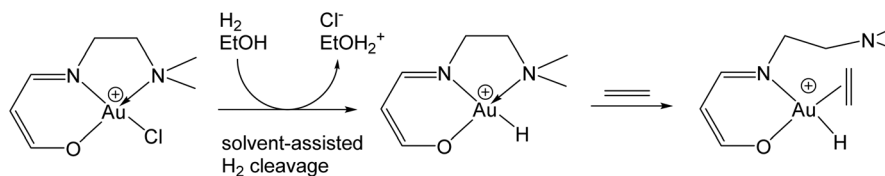
used, such as AuCl_3 .^{18,47,48} The inadvertent formation of catalytically active gold nanoparticles is also not easy to rule out. Hydride complexes such as HAuCl_2 are occasionally invoked in catalytic cycles,⁴⁹ but as yet no such species has actually been identified. Schiff-base gold(III) complexes, supported and unsupported, proved to be potent catalysts for the hydrogenation of diethyl itaconate, comparable in activity to palladium catalysts. The process of hydrogen activation (heterolytic, ethanol-assisted) and the likely intermediacy of Au(III) hydride species was explored by computational methods. Square-planar Au(III) hydride and hydrido-ethylene complexes are energetically favoured; the alternative formation of a 5-coordinate $[(\text{O}^-\text{N}^-\text{N})\text{AuH}(\text{C}_2\text{H}_4)]^+$ species was disfavoured by an increased energy barrier (Scheme 7).⁵⁰ This confirms the general picture that, although Au(III) complexes with coordination numbers 5 and 6 are not unknown,⁵¹ the square planar geometry is strongly preferred. There was, however, no experimental evidence that the postulated species could actually be detected.

Polydentate ligands offer the possibility of stabilising complexes kinetically and may also shift the redox potentials sufficiently to allow isolation and characterisation of such elusive hydride species. Cyclometallated mono- and diarylpyridine ligands provide particular stability; *e.g.* 2,6-diphenylpyridine derivatives form $\text{C}^-\text{N}^+\text{C}$ bonded pincer complexes with



Scheme 6 Computational modelling of Au(I) mediated hydrogenation steps (L = IPr).





Scheme 7 Computational models for proposed intermediates in alkene hydrogenation catalysed by Au(III) Schiff base complexes.⁵⁰

Au(III). An example is the gold hydroxide **11** which has proved to be a highly versatile starting material; for example, it undergoes aryl transfer reactions with boronic acids in toluene under neutral conditions and C–H activates fluoroarenes, to give photoluminescent gold aryl complexes in essentially quantitative yields.⁵² Surprisingly, the reaction of **11** with “superhydride”, LiHBEt₃, at –78 °C followed by stirring at room temperature proceeds without reduction of the metal centre and gives the gold hydride **12** as a yellow crystalline complex, the first example of an isolable Au(III) hydrido complex (Scheme 8).⁵³

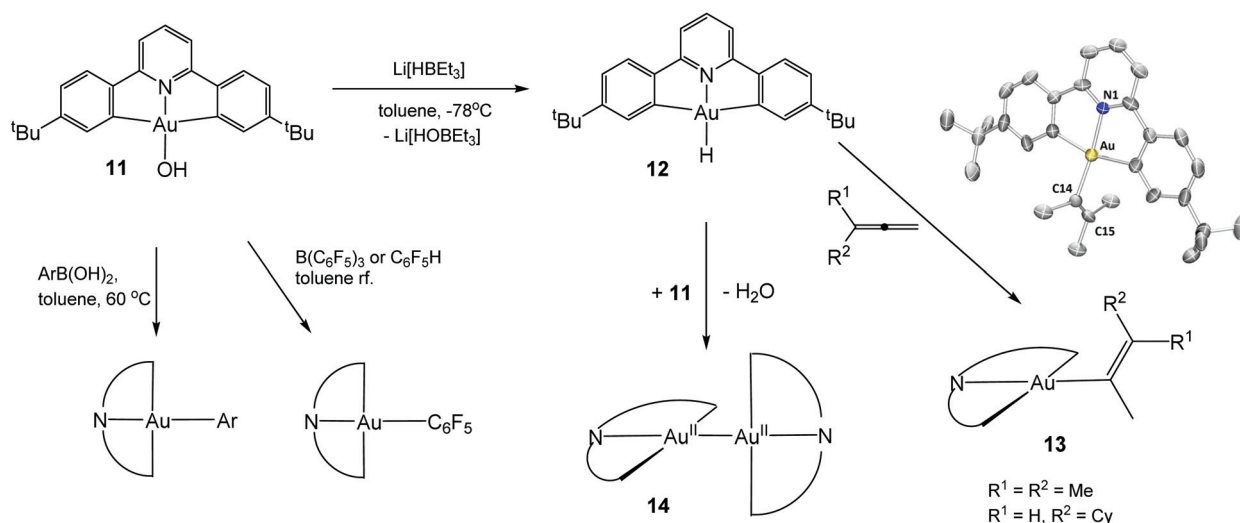
The complex was crystallographically characterized and the gold-bound H atom was located in the electron density map. The infrared spectrum of the compound shows a sharp $\nu_{\text{Au-H}}$ band at 2188 cm^{–1}. This is higher than the value for (IPr)AuH (1976 cm^{–1}) but comparable to the frequencies assigned to AuH and (H₂)AuH in an argon matrix (2226.6 and 2173.6 cm^{–1}, respectively). In the ¹H NMR spectrum the hydride ligand gives rise to a broad singlet at δ –6.51 in CD₂Cl₂ and at δ –5.73 in C₆D₆. The deuteride shows a ²H NMR resonance at δ –6.58 (CD₂Cl₂).⁵³

The observed Au–H ¹H NMR chemical shift for **12** is in line with theoretical predictions (taking relativistic effects into account), which show that systems with fully filled d-shell are dominated by deshielding spin–orbit coupling and signals are therefore found at low field, (e.g. the Au(I) complexes 4–6),

whereas for d⁸ systems the spin–orbit coupling is strongly shielding, resulting in hydride resonances high-field of TMS,⁵⁴ as is indeed observed. The chemical shift therefore does not allow any conclusions to be drawn concerning the polarity or “hydridic” character of the Au–H bond.

The Au(III) hydride **12** is stable to air and moisture at ambient conditions, an indication of the highly covalent character of the Au–H bond. The compound was found to be moderately light sensitive, and exposing CH₂Cl₂ solutions to sunlight for a few hours leads to chloride abstraction from the solvent, with formation of (C[^]N[^]C)AuCl. Complex **12** does not reduce CO₂ or benzaldehyde in the dark or under photolytic conditions, and attempted insertion reactions with ethylene, 3-hexyne, phenylacetylene, and even dimethyl acetylenedicarboxylate were unsuccessful. However, it does react with allenes under 1,2-insertion to give isolable Au(III) vinyl complexes.

Hydride **12** is stable to acetic acid. However, treating dichloromethane or toluene solutions with the strong Brønsted acid [H(OEt₂)₂][H₂N{B(C₆F₅)₃}₂]⁵⁵ at –70 °C led to the disappearance of the hydride resonance, together with signals that resembled the product of cleavage of one of the Au–phenyl bonds, [as for example in (HC–N[^]C)Au(C₆H₄F)(O₂CCF₃)⁵⁶]. Resonances that could be assigned to H₂ were not observed. Similarly, upon reacting the deuteride **12**-D with [H(OEt₂)₂][H₂N{B(C₆F₅)₃}₂] or trifluoroacetic acid at



Scheme 8 Formation and reactivity of (C[^]N[^]C)Au^{III}H.



−70 °C gave no evidence of the characteristic triplet of HD. The major product on warming to room temperature was the free 2,6-diphenylpyridine ligand.⁵⁷ It is evident that H⁺ attack takes place on the Au–C(phenyl) bond in preference to the hydride, in agreement with the covalent nature of the Au–H bond in **12**.

A more unusual reaction of **12** occurs if excess (C[^]N[^]C) AuOH is present: water is eliminated in a slow reductive condensation reaction, to give the gold–gold bonded dimeric Au(II) complex **14**, a rare example of a thermally stable Au(II) complex with an unsupported Au–Au bond. For comparison, the recently reported dimer [Au^{II}(CF₃)₂(py)]₂ follows the thermodynamic trend and spontaneously disproportionates in solution to give Au(I) and Au(III) products.⁵⁸ By contrast, **14** can be heated to 120 °C without decomposition, is stable to air and moisture in the solid state, and in some reactions turns out to be the unreactive end product. On UV irradiation it shows green photoluminescence. No reaction was observed between **14** and elemental sulfur in toluene (60 °C, 12 h) or with O₂ under 9 bar pressure, even though calculations suggest that O₂ insertion into the gold–gold bond is exothermic by 136 kJ mol^{−1}.⁵⁹ The lack of reactivity is most probably a reflection of the steric shielding provided by the four *t*-butyl substituents that envelope the Au–Au bond. On the other hand, iodine cleaves the Au–Au bond cleanly to give (C[^]N[^]C)AuI.

The reduction of the hydride **12** to the Au(II) dimer **14** was studied by cyclic voltammetry. **12** shows three reduction waves with peak potentials at −2.00 V (corresponding to a metal-centred Au(III) → II reduction), −2.25 V and −2.60 V vs. Fc^{+/0}, respectively. The −2.25 V wave was tentatively assigned to the reduction of a hydride-bridged species, such as [(C[^]N[^]C)Au^{II}–H–Au^{III}(C[^]N[^]C)], formed from the reaction of **12** with a (C[^]N[^]C)Au^{II} radical (Scheme 9). The reduction wave at −2.60 V corresponds to ligand based multi-electron processes. The reduction process of **12** differs from that of the hydroxide **11**, where no such binuclear intermediate could be identified, which suggested that under these conditions the Au–O bond is more readily cleaved than the Au–H bond.⁵⁹

The results also provided an estimate of the bond enthalpy difference between Au–OH and Au–H bonds in **11** and **12** (neglecting differences in solvation between hydride and hydroxide), which showed that the Au^{III}–H bond is more stable than Au–OH by ca. 19 kJ mol^{−1}. This agrees qualitatively with the bond strength trend determined by DFT calculations.⁶⁰

This energy difference has a number of consequences and makes gold chemistry distinctive from other metals (*vide infra*).

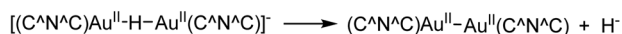
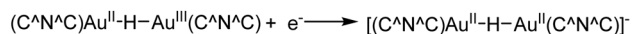
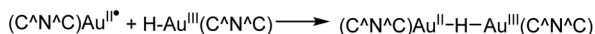
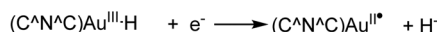
The oxidation of the dimer **14** (+0.59 V vs. Fc^{0/+}) was found to be irreversible at all voltage scan rates. This seems to suggest that the 1-electron oxidation product of the Au(II) dimer is unstable and likely undergoes rapid follow-up chemistry. There was no evidence for detectable amounts of a mixed-valence radical cation intermediate [(C[^]N[^]C)Au^{II}–Au^{III}(C[^]N[^]C)]⁺ in the oxidation process.

Electrochemistry also allowed the determination of the Au^{II}–Au^{II} bond energy of **14**. Neglecting entropic contributions, the Au^{II}–Au^{II} bond enthalpy was estimated as 198 ± 1 kJ mol^{−1}, in reasonably good agreement with DFT calculations (225 kJ mol^{−1}).⁵⁹ For comparison, Pyykkö described the Au^{II}–Au^{II} bond as a 6s6p₂5d_{xy} hybrid and calculated a bond energy of 255 kJ mol^{−1} for [Au^{II}(CF₃)₂(py)]₂.⁶¹ This suggests that the stability differences between this complex and **14** is due to kinetic rather than thermodynamic factors.

The Au–O bond

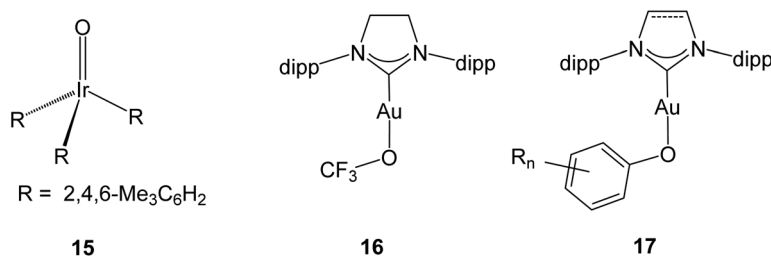
Heterogeneous gold catalysts are involved in a number of oxidation reactions, and the reaction pathways and the surface species that are likely to be involved have been the subject of numerous experimental and computational studies. Selective oxidations and the mode of O₂ activation on oxide-supported gold catalysts for CO oxidation have been reviewed.^{62,63} A number of studies are concerned with oxygen activation and the role of Au(μ-O)Au species in CO oxidation and at the Au/oxide support interface.⁶⁴ Models including Au–O–Au and Au–O–O–Au moieties have been proposed as key species in O₂ activation of supported gold catalyst supported on a variety of metal oxides.⁶⁵ Gold hydroperoxides are likely involved in the catalytic synthesis of H₂O₂,⁶⁶ as gold surface species⁶⁷ and in catalytic methanol oxidation.⁶⁸ Evidence has also been provided for peroxide and superoxide adsorbed on anionic⁶⁹ and cationic⁷⁰ gold clusters, and a variety of species including hydrides, hydroxides, peroxides and hydroperoxides are thought to be involved in propene oxidation.⁷¹ With few exceptions these proposed mechanisms and surface intermediates are based on DFT modelling. Key to rationalising all these processes is a detailed understanding of the gold–oxygen bond, including possible π-bonding contributions and preferred coordination geometries.

The nature of the metal–oxide bond has been the subject of considerable debate, notably the possibility (or impossibility) of forming terminal oxo species L_nM=O with metals in groups 9–11 (the “oxo wall”). Indeed, the only structurally confirmed example of a noble metal oxo complex is Wilkinson’s O=Ir(mes)₃ (**15**, d⁴) (Scheme 10),⁷² and there is indirect evidence for Pt^{IV}=O (d⁶).⁷³ Earlier claims of an octahedral Au(III) (d⁸) oxo species with an Au=O double bond proved to be based on error.⁷⁴



Scheme 9 Electrochemical processes in the reduction of the gold(III) hydride **12** to the Au(II) dimer **14**.⁵⁹

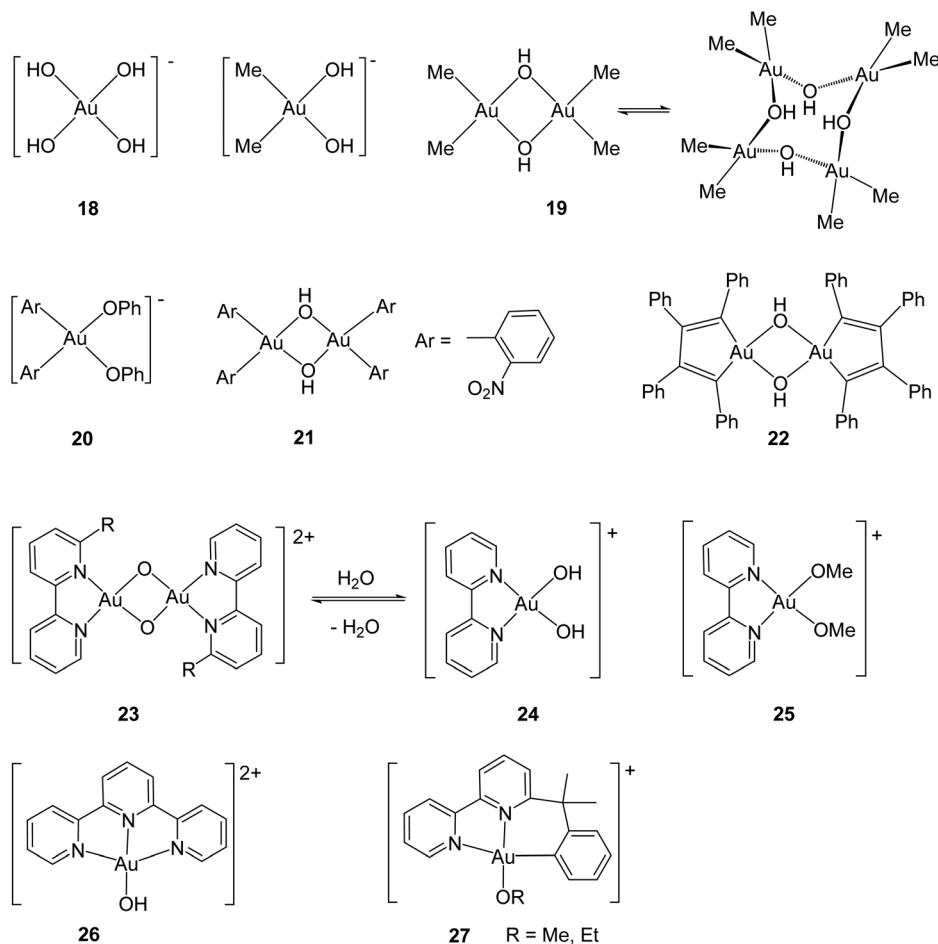




Scheme 10 Examples of metal oxo and gold(I) alkoxide complexes (dipp = 2,6- $\text{Pr}^i_2\text{C}_6\text{H}_3$).

The gold–oxygen bond in Au(I) complexes has been the subject of some detailed theoretical investigations, *e.g.* (NHC) Au–OCF₃ (**16**) which, with an Au–O–C angle of 118.3(4)°, shows little evidence of π -overlap.⁷⁵ For (NHC)Au–O–aryl complexes of type **17** it has been argued that there is interaction between the phenolate lone electron pairs and the Au–C antibonding orbital. The Au–O–C(aryl) angles are indeed much wider than expected for sp^3 hybridisation [in the range of 121.2–126(3)°], but significant steric repulsion between the bulky NHC and aryloxy ligands must be taken into account.⁷⁶

In contrast to gold(I), which prefers coordination to “soft” donors like phosphorus and sulfur, gold(III) has long been known as a “hard”, Lewis acidic metal ion. This is probably best exemplified by the square-planar tetrahydroxoaurate anion, [Au(OH)₄][−] (**18**) which forms numerous salts,⁷⁷ as well as by the classical work of Tobias concerning the identification of dimethylgold aquo ions [Me₂Au(OH₂)₂]⁺, Na[Me₂Au(OH)₂] and dimethylgold hydroxide **19** (Scheme 11). The latter is a dimer in solution but forms a tetrameric structure in the crystal, based on square-planar Me₂Au(μ -OH)₂ building



Scheme 11 Classical examples of gold(III) oxo, hydroxo and alkoxo complexes.



blocks.⁷⁸ Vicente showed that gold complexes with aryl ligands form similar compounds with Au–O bonds, including phenolate (**20**) and hydroxide (**21**) derivatives.⁷⁹ The structure of the hydroxide **22** has also been determined.⁸⁰

Like other Lewis acids, gold(III) readily forms adducts with pyridine and related N-donors, such as 2,2'-bipyridyl and terpyridyl. The formation of cyclometallated *ortho*-arylpyridine derivatives has proved a particularly successful strategy for the preparation of gold(III) complexes with oxo and hydroxo ligands. Scheme 11 shows a number of representative examples. While terminal Au=O complexes are unknown, gold(III) compounds with bridging oxo ligands are well established. In **23**, for example, the square-planar metal centres form part of a planar Au₂O₂ core, with Au–O single-bond distances of 1.976(3) and 1.961(3) Å (for R = CH₂Bu^t).⁸¹ The oxide **23** is in equilibrium with the hydroxo complex **24**.⁸² Analogous alkoxides have also been prepared and structurally characterised, such as **25**.⁸² Tridentate ligands form more stable pincer complexes and have been useful in providing dicationic terpyridyl-ligated gold hydroxides such as **26**,⁸³ as well as the cyclometallated N⁺N⁺C-bonded complexes **27**.⁸⁴

However, as of 2012 there were no reports of isolable gold complexes containing the types of O-ligands that were being postulated in heterogeneous gold-catalysed oxidations, such as superoxides Au–OO[•], peroxides Au–OO–Au, and hydroperoxides Au–OOH. We were therefore interested in the synthesis and characterisation of such compounds.

Given that the hydroxide (C[^]N[^]C)AuOH (**11**) had proved an ideal starting material for hydride synthesis (Scheme 8), we chose this compound as the starting point for reactions with peroxides. The reaction of **11** with *t*-BuOOH readily affords the alkylperoxide **28**. Similarly, treatment of **11** with H₂O₂ resulted in the rather delicate hydroperoxide **29**, which has a tendency to condense with excess **11** to give the peroxide **30**. This water elimination is reversible. Such a dehydration reaction also

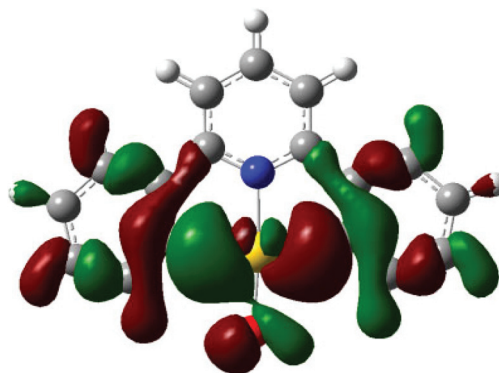
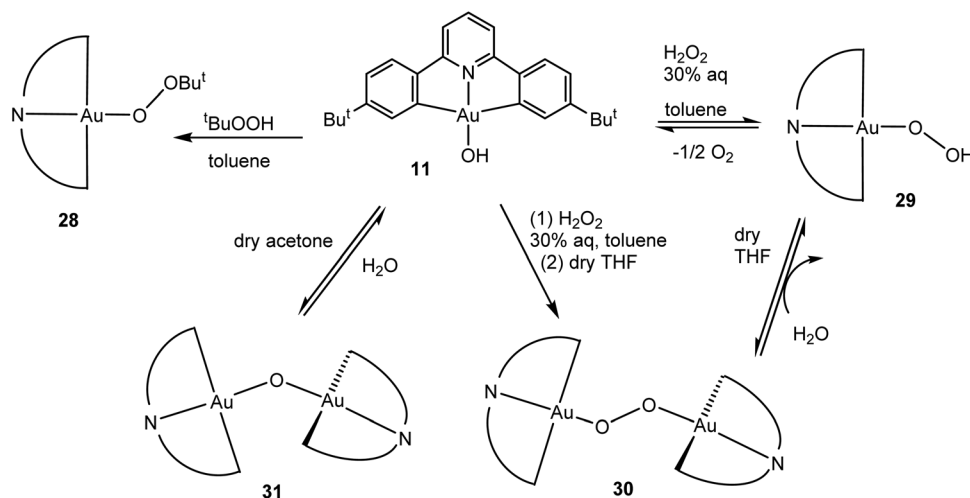


Fig. 1 HOMO–1 orbital of (C[^]N[^]C)AuOH (**11**), showing the relative phases of Au orbitals and the lone pairs of the OH ligand.

became apparent when **11** was stirred in dry solvents (*e.g.* dry acetone), which led to the formation of the μ -oxide **31** (Scheme 12). The identity of all these species was confirmed by X-ray crystallography. Oxide and hydroxide are in equilibrium, as are peroxide and hydroperoxides.⁶⁰ Subsequently a gold(I) *t*-butylhydroperoxide has also been prepared by an analogous route.⁸⁵

The crystal structure of the μ -oxide **31** also answers the question concerning possible π -bonding contributions to the Au–O interaction. With less electron-rich metals, M–O π -bonding leads to a widening of the M–O–M angle up to 180° and M–O bonds with partial double-bond character. The Au–O–Au angle in **31**, on the other hand, is 113.5°, only slightly less acute than the tetrahedral angle of 109.5°, a rather small steric effect given the bulkiness of the two (C[^]N[^]C)Au fragments. There is therefore no evidence for any interaction between the Au(III) centres and the lone pairs on the bridging O ligand. This is further borne out by DFT calculations on **11**, which show that the lobes of the gold(III) d-orbitals and of the oxygen lone pairs in the rele-



Scheme 12 Generation and interconversion of gold(III) oxide and peroxide complexes.⁶⁰



Table 1 Calculated Au–X and Pt–X bond dissociation energies (BDEs)⁶⁰ and experimental comparison data (kJ mol^{−1})

Compound ^a	BDE	On Au(111) surface ^b	Diatomic compound	BDE ^c
LAu–OH (11)	279	251		
LAu–OAuL (31)	206		Au–O	223 ± 21
LAu–OOH (29)	168	108		
LAu–OOAuL (30)	126			
LAu–H (12)	317		Au–H	292 ± 8
LAu–Me	262			
LAu–OMe	209			
(C [^] N [^] C)Pt–H	350		Pt–H	352 ± 38
(C [^] N [^] C)Pt–OH	367		Pt–O	391 ± 42
(C [^] N [^] C)Pt–Me	297			

^a L = C[^]N[^]C pincer ligand. ^b Estimates based on single-crystal absorption calorimetry, values from ref. 65c. ^c Data from: J. A. Martinho Simoes and J. L. Beauchamp, *Chem. Rev.*, 1990, **90**, 629.

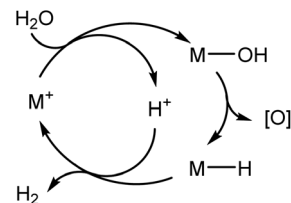
vant MO (here HOMO–1) are out of phase (Fig. 1). The same result was found for the hydroperoxide 29.⁶⁰

Attempts to generate these Au peroxide species directly from O₂ failed: neither the hydride 12 nor the Au(II) dimer 14 insert O₂, even under forcing conditions, in spite of the calculated exothermic character of the reaction. The reactivity of these (C[^]N[^]C)Au(III) pincer complexes differs therefore from the behaviour of palladium and platinum, where O₂ insertions into M–H and Pd–Pd bonds proceed with ease.^{86,87}

The reactivity of these gold(III) hydride and oxide species is in keeping with the Au–X bond energies. Pertinent values are given in Table 1.

The gold(III) hydroperoxides, peroxide and oxide species are interconvertible. Treatment of the hydroperoxides with a phosphine PAR₃ led to selective and stepwise O-atom abstraction, with formation of the phosphine oxide (Ar = 4-C₆H₄R; R = H, F, Me, OMe) (Scheme 13). Electron-donating R groups increased the reaction rate. O-abstraction from the oxide 31 generated the Au(II) dimer 14. Remarkably, even the hydroxide 11 could be deoxygenated, to give the hydride 12.

These reaction sequences are in line with the bond energy trend, Au–H > Au–O. The transformation of a metal hydroxide into a metal hydride (in the absence of a hydride transfer

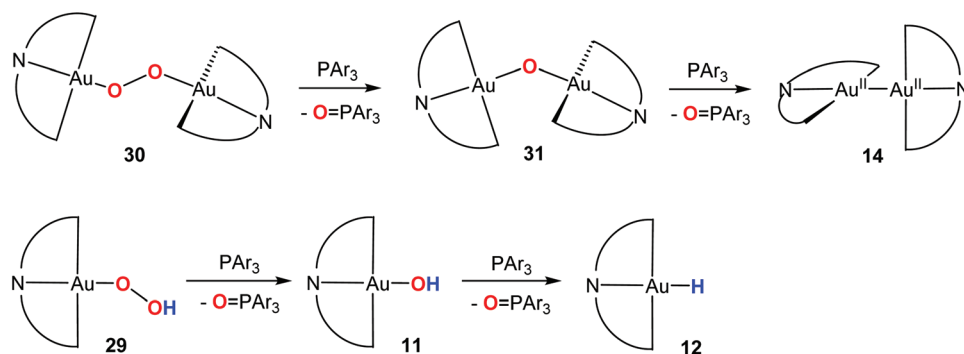
**Scheme 14** Principle of a water-splitting cycle based on M–OH deoxygenation.

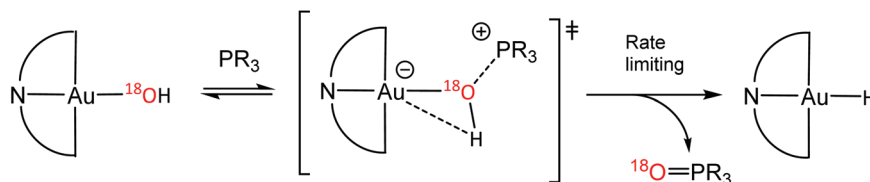
agent) is unique to Au(III) and is not known for any other metal.

For platinum(II), the order of bond energies is reversed, Pt–H < Pt–O, and the hydroxide-to-hydride transformation is thermodynamically unfavourable. This is therefore an example of a reaction which gold can do but platinum cannot. However, the energetics are very carefully balanced: whereas the Au–OH deoxygenation works for Au(III), gold(I) hydroxides like (IPr)AuOH do not react.

The hydroxide to hydride conversion is, in principle, a key step in a water splitting cycle which does not require oxidation state changes of the metal (Scheme 14). However, so far it has not been possible to close the cycle because the gold hydride is too stable and does not react with acids under H₂ elimination.

The oxygen abstraction by phosphines proceeds *via* a concerted mechanism. The kinetics (over the temperature interval –10 to –55 °C, toluene) show a secondary kinetic isotope effect $k_H/k_D = 1.45$, consistent with an Au–O–H bending motion in the rate limiting step. DFT studies confirmed that the oxygen is abstracted *via* an external attack by phosphine (PMe₃ as model); intermediates involving a 5-coordinate phosphine adduct of gold could not be identified. ¹⁸O-labelling confirmed that the phosphine oxide formed was derived from the gold hydroxide. The reaction is 1st order in both [Au] and [PR₃]; the kinetic parameters ($E_a = 31.4 \pm 1.7$ kJ mol^{−1}; $\Delta H^\ddagger = 35.02(67)$ kJ mol^{−1}; $\Delta S^\ddagger = -105.9(3)$ J mol^{−1} K^{−1}) show a strongly negative entropy of activation, in agreement with an associative mechanism. The rates for different phosphines

**Scheme 13** Oxygen transfer reactions of Au(III)–O complexes.



Scheme 15 Proposed mechanism for O-abstraction from Au^{III}–OH by phosphines.

with electron donating and withdrawing *para*-substituents follow a Hammett relationship ($\rho = -3.15$), with electron-donating groups such as Me or OMe accelerating the rates substantially. The negative ρ value (-1.05 per aryl ring) suggests that positive charge is built up on the reaction centre and is in good agreement with a zwitterionic transition state (Scheme 15).⁶⁰

In summary, studies in gold(III) oxide systems have confirmed the absence of double-bond character and of π -bonding contributions in the Au–O bond. The first examples of gold peroxides and hydroperoxides have been isolated. The Au–OO bond is substantially weaker than the Au–O(oxide) and Au–OH bonds, and all of these are weaker than the Au–H bond. Both Au(I) and Au(III) hydrides are highly covalent species, stable to air and moisture and surprisingly resistant to weak acids. One interesting consequence of these bond energy differences was the facile O-abstraction from a gold(III) hydroxide to give the corresponding gold hydride, a reaction that is so far unique to Au(III) and found neither for Pt(II) nor for Au(I).

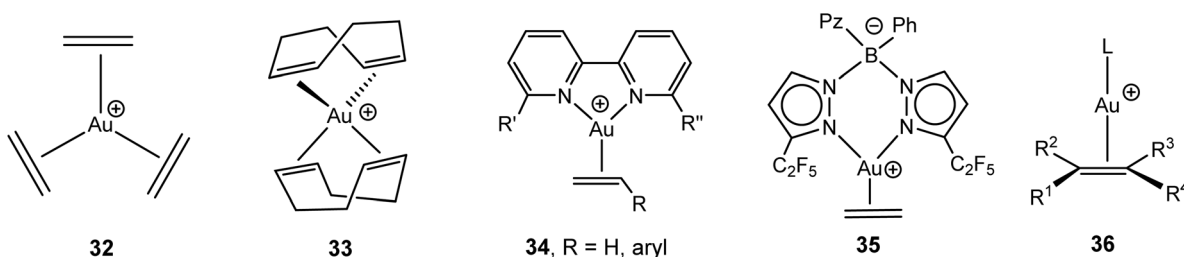
Gold π -complexes of alkenes and alkynes

The chemistry of π -complexes of gold in various oxidation states with alkenes and alkynes has recently been the subject of a very detailed and comprehensive review.⁸⁸ Only a brief summary of the main complex types needs to be given here. The first alkene adducts of AuCl were reported in the 1960s by Chalk⁸⁹ and Hüttel;⁹⁰ the latter developed this chemistry throughout the 1970s and 80s.⁸⁸ The advent of very non-

coordinating anions made it possible to isolate complexes where Au(I) is exclusively ligated to alkenes, as in the trigonal-planar [Au(C₂H₄)₃]⁺ (32), [Au(norbornene)₃]⁺ and tetrahedral [Au(COD)₂]⁺ cations (COD = 1,5-cyclooctadiene) (33) (Scheme 16).^{91–93} The reaction of the gold(III) oxide [Au₂(μ -O)₂(bipy)₂]²⁺ with alkenes proceeds with reduction to give the Au(I) bipyridyl-stabilised alkene complexes of type 34 (bipy = variously 6,6'-substituted bipyridyl), with alkene = styrene, *p*-methoxystyrene, α -methylstyrene, *cis*-stilbene; the complexes with norbornadiene, COD and dicyclopentadiene are alkene-bridged binuclear species.⁹⁴ Tris(pyrazolato)borates act as bidentate N-donor ligands in the zwitterionic complex 35.⁹⁵

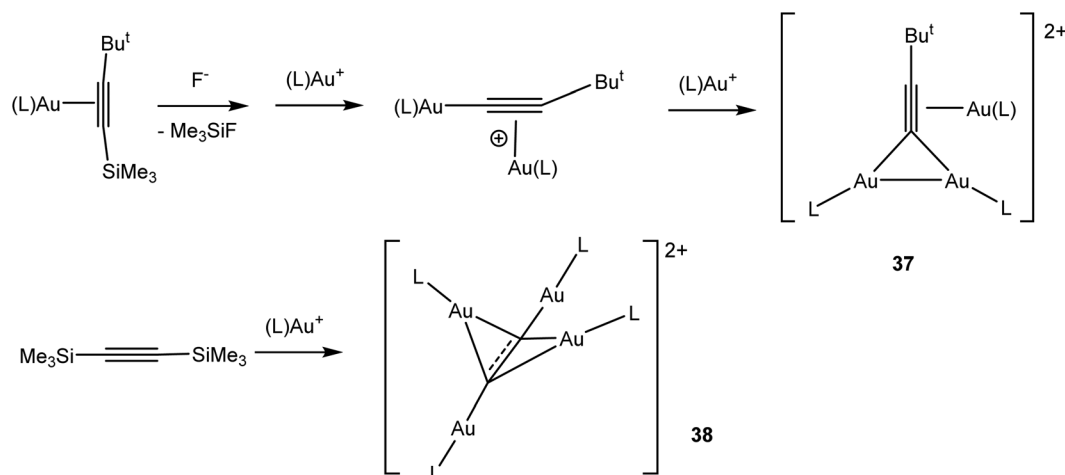
Strongly donating phosphine and NHC ligands have proved useful in stabilising two-coordinate Au(I) complexes of type 36. These complexes have recently been reviewed.⁹⁶ Complexes with alkenes carrying 1–4 substituents are now known, including the crystallographically characterised isobutene (L = IPr) and tetramethylethylene derivatives (L = Bu^t₂PC₆H₄-2-Ph).^{97,98} Structurally similar complexes have been reported for 1,3-dienes, which are η^2 -coordinated, as well as for cyclic dienes, allenes,⁹⁹ and vinyl ethers.¹⁰⁰ An η^2 -cyclopentadiene complex of type 36 has also been characterised (L = Bu^t₂PC₆H₄-2-Ph), and mixtures of Ph₃PAuCl and AgSbF₆ were found to polymerise cyclopentadiene and 1,3-cyclohexadiene. A mechanism was not suggested, although Au⁺ or H⁺ initiated carbocationic diene polymerisation seems most likely.¹⁰¹

The structural chemistry of gold(I) alkyne complexes follows the pattern set out for alkene adducts and was recently discussed in detail by Schmidbaur.⁸⁸ The involvement of Au(I) alkyne compounds in homogeneous gold catalysed alkyne reactions has been reviewed.¹⁰² Two-coordinate adducts prevail, and complexes of cyclic alkynes tend to be the most



Scheme 16 Types of Au(I) alkene complexes.



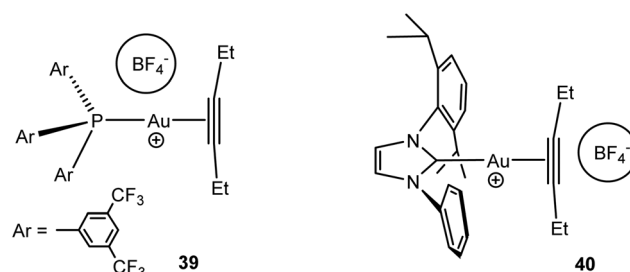


Scheme 17 Formation of oligonuclear cationic gold alkyne complexes ($L = \text{PBu}_3^t$).¹⁰⁷

stable due to the stronger π -interactions of strained $\text{C}\equiv\text{C}$ bonds with metal centres.^{103–105} Complexes of AuCl with non-cyclic alkynes tend to be thermally sensitive. It has proved possible to crystallographically characterise the 3-hexyne complex $\text{AuCl}(\text{EtC}\equiv\text{CEt})$, which shows a $\text{C}\equiv\text{C}$ bond length of 1.224(6) Å, only marginally longer than that of a typical non-coordinated alkyne (around 1.202 Å).¹⁰⁶ In line with this very small degree of bond elongation, structural and DFT studies on $\text{Au}(\text{i})$ complexes with cyclic alkynes have shown that $\text{C}\equiv\text{C}$ π -donation into the σ^* orbital of the Au-L bond ($L = \text{NHC}$) is 3–4 times larger than $d(\text{Au}) \rightarrow \pi^*(\text{C}\equiv\text{C})$ back-donation. These observations explain the electrophilic activation of alkynes by LAu^+ fragments in gold(i) catalysed reactions. Surprisingly, AuCl proved to be both the strongest donor and the strongest acceptor.¹⁰⁴ With silyl alkynes, desilylation has been observed, which leads to a number of structurally characterized oligonuclear complexes (37),¹⁰⁷ not dissimilar to the interactions postulated for di-gold activation of alkynes.¹⁰⁸ Desilylation of bis(silyl) acetylene gave a tetranuclear dication 38 (Scheme 17).

NMR spectroscopic studies (^1H – ^{19}F HOESY experiments) showed that the relative cation–anion positions in gold(i) alkyne complexes $[(\text{L})\text{Au}(\text{alkyne})]^+\text{BF}_4^-$ have been found to vary, depending on the ligand structure; the anion is located close to gold in the phosphine complex 39 but has close interactions with the alkyne ligand in the NHC derivative 40 (Scheme 18). DFT studies showed that the phosphine complex in this case is the stronger π -acceptor.¹⁰⁹ Anions also play an important role in the intermolecular alkoxylation of alkynes catalysed by carbene-based gold(i) salts, $(\text{NHC})\text{AuX}$ ($\text{X}^- = [\text{B}\{\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4]^-$, BF_4^- , OTf^- , OTs^- , TFA^- , or OAc^-). The anion is involved in alcohol deprotonation, and the intermediate basicity of the OTs^- anion gave the most efficient catalysis.¹¹⁰

In addition to the mono-alkyne adducts of AuCl and $[(\text{L})\text{Au}]^+$, the bis- and tris-alkyne compounds 41–43 have also been characterised (Scheme 19). The structures are analogues of alkene adducts, but the tris-cyclooctyne complex 42 shows a

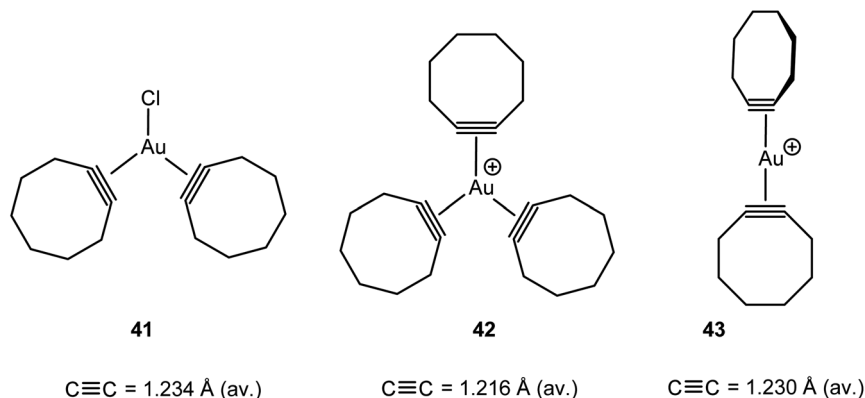


Scheme 18 Ion pair structures of gold alkyne complexes.¹⁰⁹

slight propeller-type twist of the ring ligands, with torsion angles of 3.0, 6.3 and 43.9°. The Au-C bond lengths to the cyclooctyne with the largest twist are significantly larger than the Au-C bonds to the other, in-plane, ligands. This indicates weaker bonding of one of the alkyne ligands, and indeed on recrystallization some alkyne is lost and crystals of the bis-alkyne adduct could also be obtained. In the $[\text{Au}(\text{cyclooctyne})_2]^+$ cation 43 the alkyne ligands are oriented almost perpendicular to one another. The $\text{C}\equiv\text{C}$ bonds in these compounds are slightly elongated compared to the corresponding free alkynes, with the largest elongation being displayed by the neutral AuCl adduct, which can be expected to display the strongest back-donation.¹¹¹

So far it has not been possible to isolate alkyne complexes of gold(III). Early attempts to react disubstituted alkynes with AuCl_3 led to reduction.⁸⁸ Interestingly, in NMR studies on the reaction of the thermally unstable gold(III) diaryl complex $[(\text{C}_6\text{F}_5)_2\text{AuCl}]_2$ at -80 to 0°C Laguna *et al.* were able to detect some tantalising indications for the formation of an alkyne complex with the tentative structure $(\text{C}_6\text{F}_5)_2\text{AuCl}(\eta\text{-PhC}\equiv\text{CH})$ ($\delta^1\text{H}$ 3.76, toluene- d_8). However, on removal of the solvent above -50°C the compound decomposed to metallic gold.¹¹²





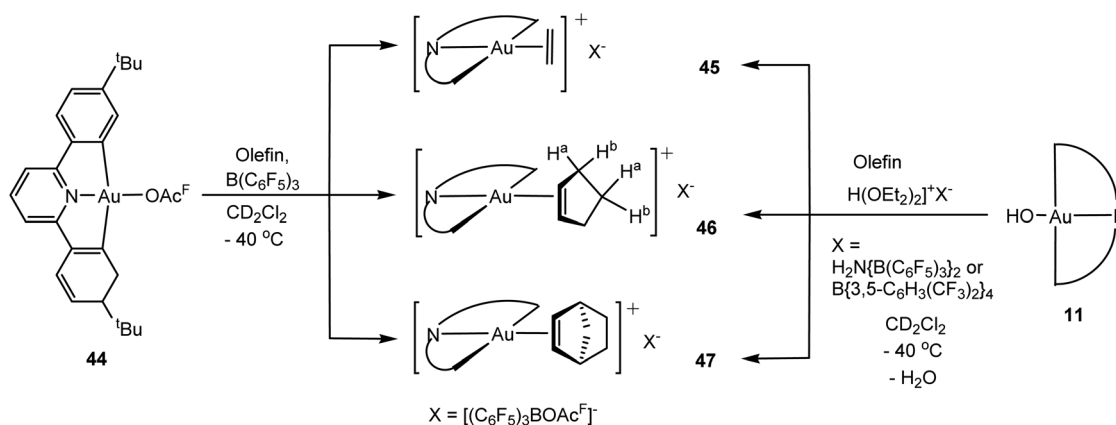
Scheme 19 Structurally characterised bis- and tris-cyclooctyne complexes of gold(I).¹¹¹

By contrast to alkynes, the first examples of alkene complexes of gold(III) have recently been reported, by two very different routes. Initial attempts seemed to confirm the susceptibility of gold(III) alkene species to reduction; for example, efforts to displace the ether ligands in Uson's bis(pentafluorophenyl)gold(III) cation¹¹³ $[(C_6F_5)_2Au(OEt_2)_2]^+$ with norbornene or 1,5-cyclooctadiene were unsuccessful, while chloride abstraction from $[(C_6F_5)_2AuCl_2]^-$ with $AgSbF_6$ in the presence of norbornene led to reductive elimination of perfluorobiphenyl and formation of $[Au(norbornene)_3]^+$. The strategy of taking advantage of the stability of the C[∧]N[∧]C pincer ligand framework proved more successful. The trifluoroacetate ligand in (C[∧]N[∧]C)Au(OAc^F) (44) is easily abstracted by $B(C_6F_5)_3$ in dichloromethane, and adding alkenes to this solution at $-40\text{ }^\circ\text{C}$ resulted in the clean formation of the corresponding η^2 -alkene complexes 45–47 (Scheme 20).¹¹⁴

Dichloromethane solutions of the cyclopentene and ethylene complexes are stable up to about 0 and $-20\text{ }^\circ\text{C}$, respectively, whereas solutions of the norbornene complex 47 can be handled at $20\text{ }^\circ\text{C}$. Removal of volatiles afforded the complexes

as yellow powders which can be stored indefinitely under nitrogen. Once isolated, these complexes proved stable in the solid state for hours at room temperature and in air with minimal degradation.

In the absence of excess ethylene, complex 45 shows a sharp ^1H NMR singlet at δ 6.29, *downfield* shifted from the δ 5.38 signal of free C_2H_4 (CD_2Cl_2 , $-40\text{ }^\circ\text{C}$), in contrast to Au(I) and Pt(II) ethylene complexes, which show an *upfield* shift of the ethylene resonance (Table 2), suggestive of π -electron donation which is poorly compensated by back-bonding. In the presence of excess ethylene the ^1H NMR signals broaden on warming from -70 to $-10\text{ }^\circ\text{C}$, as expected for ligand exchange. The $^{13}C_2H_4$ complex shows a $^{13}C\{^1H\}$ NMR resonance at δ 108.9, up from δ 122.8 for the free alkene; J_{CH} increased on coordination from 156 to 166 Hz. Similar J_{CH} values have been found for gold(I) ethylene complexes, although in those cases the changes in the ^{13}C NMR chemical shifts $\Delta\delta$ (^{13}C) are much larger, of the order of 60+ ppm, for both Au(I) and Pt(II). The Au(III)–alkene bond is evidently weaker, particularly the back-bonding contribution, than the Pt(II)–alkene bond.



Scheme 20 Synthesis of gold(III) alkene complexes.

Table 2 Comparison of NMR data^a of selected gold(II), platinum(II) and gold(III) alkene complexes

Compound	$\delta^1\text{H}$	$\Delta\delta$ (H)	$\delta^{13}\text{C}$	$\Delta\delta$ (C)	J_{CH} [Hz]	Ref.
C_2H_4	5.38		122.8		156	
$[\text{Au}(\text{C}_2\text{H}_4)_3]\text{SbF}_6$	4.94	−0.44	92.7			91a
$\text{HB}(\text{pz}^{\text{CF}_3})_3\text{Au}(\text{C}_2\text{H}_4)^{\text{b,c}}$	3.81	−1.6	63.7	−59.8	165	95
$[(\text{bipy}^{\text{R}})\text{Au}(\text{C}_2\text{H}_4)]\text{PF}_6^{\text{d}}$	3.09	−2.3	61.6	−55.2		94b
$\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]^{\text{e}}$	4.83	−0.55	67.1	−55.7		115 and 116
$[\text{MePt}(\text{PMe}_2\text{Ph})_2(\text{C}_2\text{H}_4)]\text{PF}_6$	4.12	−1.26	84.8	−38.4		116 and 117
45	6.29	0.91	108.9	−13.9	166	114
<i>trans</i> -(py)PtCl ₂ -(cyclopentene)	6.23	0.49				118
46	6.30	0.56				114

^a In CD_2Cl_2 unless indicated otherwise. ^b $\text{pz}^{\text{CF}_3} = 3,5\text{-(CF}_3)_2\text{pyrazolate}$. ^c In CDCl_3 . ^d $\text{bipy}^{\text{R}} = 4\text{-(2'',6''-Me}_2\text{C}_6\text{H}_3\text{)-2,2'-bipyridyl}$. ^e In 1 M methanolic HCl. The chemical shift of free C_2H_4 in this solvent is δ 5.37.

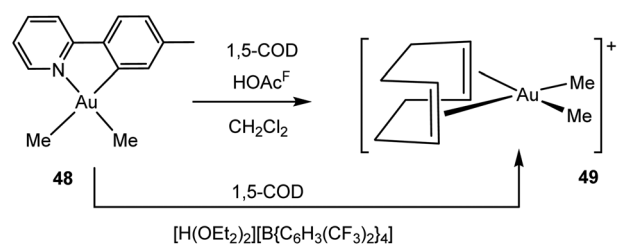
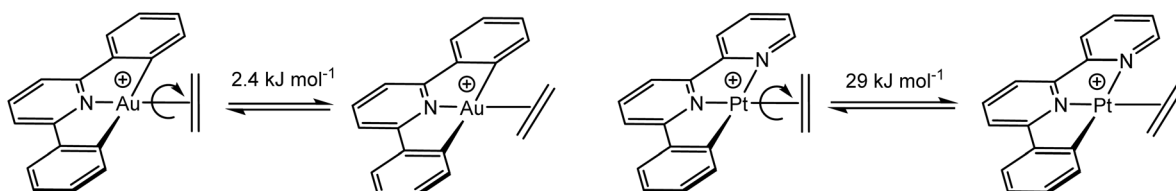
This remarkably low Au(III)–ethylene back-bonding contribution, compared to Pt(II), is further underlined by the calculated rotational barriers. The energy difference for the in-plane and perpendicular ethylene orientations for **45** was estimated to be only 2.4 kJ mol^{−1}, less than 10% of the value for isostructural cationic platinum pincer compounds (Scheme 21). This agrees with the donation/back-donation (d/b) ratio obtained by charge decomposition analysis, which gives a value of d/b = 3.41 for Au(III) but d/b = 1.70 for Pt(II), *i.e.* back-donation is much more important for platinum than for gold.¹¹⁹ This general picture, *i.e.* the remarkably small contribution of back-bonding for Au(III), has since been confirmed for other systems, including chelating olefin and CO complexes (*vide infra*).

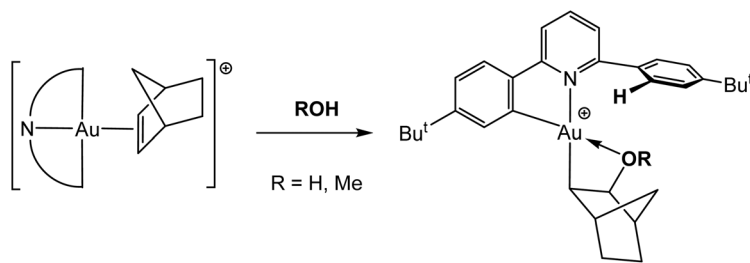
Cyclopentene coordination in **46** was indicated by a downfield shift of the olefinic proton signal from δ 5.74 to 6.3 ppm, as well as by the inequivalence of the methylene protons. There was no indication of ligand exchange, which would have resulted in the interchange of the methylene-protons H_a and H_b (Scheme 20); the CH₂ groups of η^2 -cyclopentene are diastereotopic, and coordination is *via* one π -face only.

Unlike the cyclopentene and ethylene compounds, the CH=CH signal of the norbornene complex **47** shows only a small upfield shift from δ 6.02 to 5.8; in this case a clearer indication of C=C coordination is provided by the bridgehead CH signals, which are shifted from δ 2.84 for free norbornene to δ 3.49.¹¹⁴

A different route to an Au(III) alkene complex was developed by Tilset and co-workers, by reacting the cyclometallated dimethylgold complex **48** with trifluoroacetic acid at −78 to 0 °C in the presence of COD.¹²⁰ Under these conditions the phenyl-

pyridine ligand is displaced, to give *cis*-[Me₂Au(COD)]⁺ (**49**) (Scheme 22). The same cation is formed by protonating **48** with [H(OEt₂)₂][B{C₆H₃(CF₃)₂]₄]. Borate salts of **49**⁺ proved suitable for X-ray diffraction. The olefinic ¹H NMR signal is found at δ 6.39, 0.8 ppm higher than the signal of free COD. The Au–C bonds to the COD ligand are considerably longer than the Pt–COD bonds in the analogous platinum complex (1,5-COD) PtMe₂ (average Au: 2.389; Pt: 2.228 Å), while the C=C bond lengths in both complexes are identical within experimental error (average Au: 1.356(5); Pt: 1.355(17) Å); both show slight elongation compared to free 1,5-COD [C=C 1.340(3) Å]. The Au–C bond length to the two C-atoms of the same C=C bond differ by over 0.04 Å, a consequence of conformational strains in the COD backbone. DFT modelling showed that back-bonding from the metal d_{xz} and d_{yz} orbitals is substantially weaker for Au(III) than for Pt(II); this reinforces the bonding picture suggested by the spectroscopic results for compounds **45**–**47**.

**Scheme 22** Synthesis of Au(III) COD complexes.¹²⁰**Scheme 21** Rotational barriers in Au(III) and Pt(II) ethylene complexes.



Scheme 23 Reaction of the gold(III) norbornene complex **47** with protic reagents.¹¹⁴

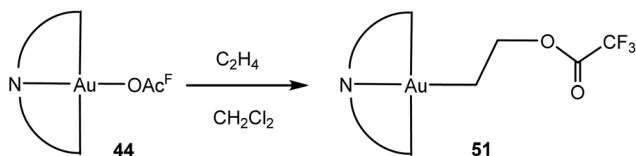
The coordinated C=C bonds in Au(III) complexes are very susceptible to nucleophilic attack. The norbornene complex **47** was found to react with traces of moisture or with alcohols to give the corresponding hydroxy- or alkoxyalkyl complexes **50**, respectively (Scheme 23). The reaction involves the protolytic cleavage of one of the Au–phenyl bonds of the pincer ligand. The OH-derivative was structurally characterized (as SbF₆[−] salt).¹¹⁴

An unusual reaction that was discovered in the course of this work is the direct insertion of ethylene into the Au–trifluoroacetate bond, to give the crystallographically characterised 2-acetatoethyl complex **51** (Scheme 24). The insertion proceeds slowly (14–72 h) at room temperature and is quantitative; it is accelerated by AgOAc^F impurities which catalyse the acetate abstraction.¹¹⁴ The reaction is yet another expression of the thermodynamic trend in Au^{III}–O and Au^{III}–C bond strengths (*cf.* Table 1).

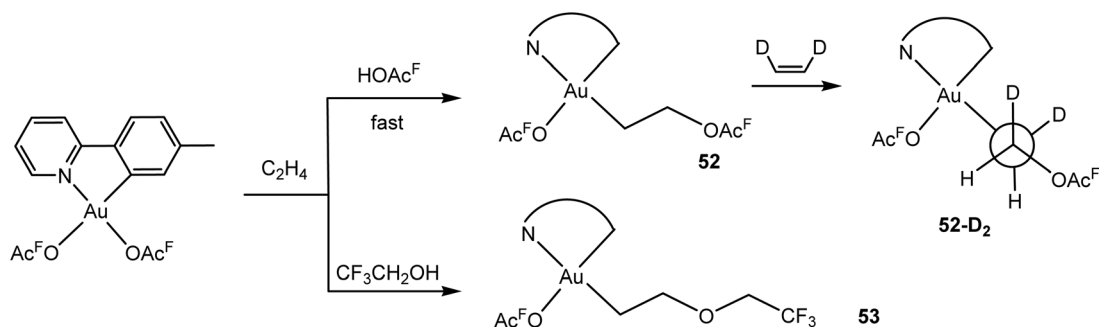
The mechanism of ethylene insertion into gold(III)–trifluoroacetate bonds was subsequently investigated in detail by

Tilset and co-workers.¹²¹ In trifluoroacetic acid as the solvent the ethylene insertion is fast (5–30 min). There is a strong kinetic preference for insertion *trans* to the N-donor. The reaction is reversible, and there is ethylene exchange with C₂D₄. With Z-C₂H₂D₂ the *threo* isomer **52-D₂** is formed, arising from external *anti* attack by acetate on ethylene in the likely intermediate [(C[^]N)Au(OAc^F)(η²-C₂H₄)]⁺; this ethylene complex itself could however not be detected. In trifluoroethanol as solvent the corresponding 2-alkoxyethyl complex **53** is formed (Scheme 25).

Whereas alkene insertions into Au–X bonds lead to functionalised alkyls, the formation of new C–C bonds requires alkene insertion into a gold–alkyl bond. These are generally not at all facile. As Amgoune and Bourissou were recently able to show, such a pathway becomes feasible if a coordinatively unsaturated, formally three-coordinate gold(III) species can be generated. This was successful in the case of the cyclometalated phosphinonaphthalene complex **54** (Scheme 26).¹²² While cold (−80 °C) mixtures of **54** with B(C₆F₅)₃ as methide abstractor failed to react with ethylene or styrene and gave Au–C₆F₅ species on warming, the reaction with norbornene led to the first observation of an alkene insertion into a gold(III) alkyl bond. The addition of neutral N-donors allowed the isolation of **55**, while chloride addition afforded the crystallographically characterised complex **56**. The *syn*-1,2 character of the insertion process suggests an intramolecular migratory pathway *via* an (undetected) alkene complex [(C[^]P)AuMe(η²-norbornene)]⁺ as the intermediate.¹²³

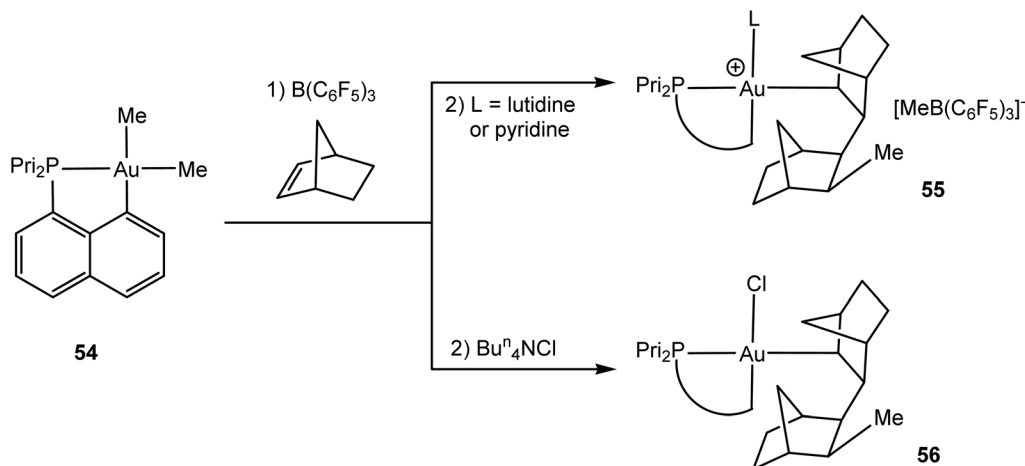


Scheme 24 Ethylene insertion into the gold–trifluoroacetate bond.¹¹⁴



Scheme 25 Ethylene insertion in (C[^]N)Au(OAcF)₂ complexes.¹²¹





Scheme 26 Norbornene insertion into an Au–Me bond.¹²²

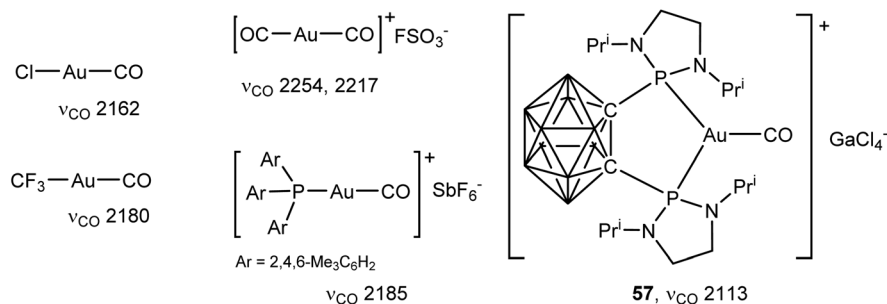
The picture that has emerged is that Au(III) alkene complexes can indeed be isolated and characterized, over 180 years after the first preparation of the famous Pt(II) analogue, Zeise's salt. They differ however substantially from the alkene complexes of both Au(I) and Pt(II) in terms of bonding and reactivity and rely almost entirely on the (C=C)→Au(III) donor interaction, with very little back-bonding contribution and very low rotational barriers. This makes gold(III) alkene compounds highly susceptible to nucleophilic attack, even by traces of moisture or weak nucleophiles such as trifluoroacetate in acidic media. As yet there are no examples of isolable gold(III) alkyne adducts, most likely because alkyne complexes rely for stability even more on π -back-donation.

CO complexes

The first carbonyl complex of gold was Manchot's AuCl(CO), first reported in 1925.^{124,125} Since then a number of neutral^{126–130} and cationic^{128–134} CO complexes of gold(I) have been described. The bonding of CO to gold in compounds of the type [(L)Au^I(CO)]⁺ (L = phosphine or NHC) has recently been analysed in detail.¹³⁵ These complexes are linear. In

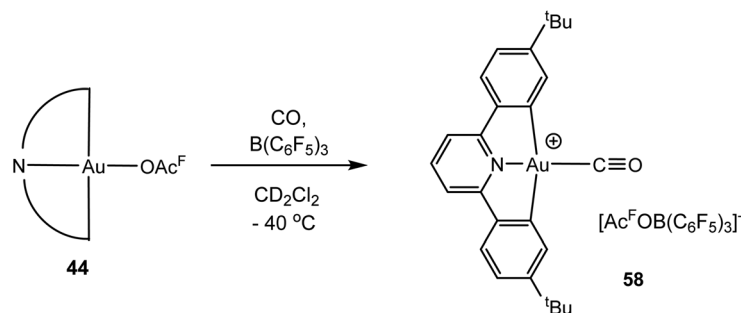
gold–CO complexes the donation of the non-bonding electron pair on carbon dominates over back-donation, which leads to an increase of the CO stretching frequency to a value higher than that of free CO (2143 cm^{−1}) and more akin to the formyl cation HC≡O⁺ (2184 cm^{−1}), a situation found for quite a number of highly electrophilic metal ions (often referred to as “non-classical CO complexes”,¹³⁶ a term that is not without objections¹³⁷). For linear gold complexes [(L)AuCO]⁺ it was shown that the ν_{CO} stretching frequencies do not correlate readily with the familiar Tolman electronic parameters of the L ligands; instead the ν_{CO} frequencies are mainly determined by the flux of π -electron density from the L–Au bond.¹³⁵ A three-coordinate CO complex with a chelating carboranyl bis(phosphine) ligand, [(P[^]P)Au–CO]⁺ (57), has also been reported; here the increased electron density provided by the chelating phosphine increases the π -back-bonding sufficiently to give the first “classical” gold CO complex (ν_{CO} = 2113 cm^{−1}) (Scheme 27).¹³⁸ The situation resembles that in the three-coordinate styrene complex 34, which also shows stronger back-bonding than two-coordinate alkene complexes.⁹⁴

The CO complexes of gold(I) are mainly interesting from a bonding perspective. Since the metal has a full complement of d-electrons and there are no energetically accessible orbitals



Scheme 27 Representative types of Au(I) CO complexes, with ν_{CO} stretching frequencies (cm^{−1}).^{128,129,133,138}





Scheme 28 Synthesis of Au(III) CO complexes.

cis to CO, Au(I) carbonyls do not participate in carbonylation catalysis.¹³⁹ On the other hand, Au–CO adducts are likely involved in heterogeneous gold catalysis, including the much-studied catalytic oxidation of CO^{64,65} and of methanol.^{67,68} This includes surface species of TiO₂-supported CO oxidation catalysts where gold is thought to be present as Au³⁺ ions; and CO adducts with $\nu_{\text{CO}} = 2158 \text{ cm}^{-1}$ have been identified.¹⁴⁰

However, isolable CO complexes of gold in the oxidation state +III were unknown. Indeed, as early as 1905 it was reported¹⁴¹ that treating HAuCl₄ with CO leads to reduction and is in fact an excellent method for the preparation of colloidal gold nanoparticles; this method continues to be used for this purpose.¹⁴²

Given that Au(III) and Pt(II) are isoelectronic and Pt(II) provided the first transition metal carbonyl complex ever made, PtCl₂(CO)₂ (1868),¹⁴³ the lack of isolable Au(III) CO complexes is rather surprising. Redox potentials can of course be shifted by suitable ligands, and in spite of the reducing power of CO, we found recently that CO complexes of Au(III) are in fact readily accessible. Thus, treating mixtures of (C[^]N[^]C)Au(OAc^F) (44) and B(C₆F₅)₃ in dichloromethane at –30 °C with CO generates [(C[^]N[^]C)Au–CO]⁺[(C₆F₅)₃BOAc^F][–] (58) (Scheme 28).¹⁴⁴ The complex can be isolated by precipitation with light petroleum as a yellow microcrystalline solid. [(C[^]N[^]C)Au–¹³CO]⁺ (58-¹³C) was obtained similarly and gives a ¹³C NMR resonance at δ 167.6 (*cf.* δ 184 for free CO). The same product was obtained when [(C[^]N[^]C)Au(C₂H₄)]⁺[(C₆F₅)₃BOAc^F][–] (45) was exposed to CO. The CO complex is thermally labile, and solutions must be kept <–10 °C. The ν_{CO} stretch of 58 was observed at 2167 cm^{–1} (58-¹³C: 2143 cm^{–1}). This value is rather close to that of CO bound to Au³⁺ centres on titania-supported gold mentioned above (2158 cm^{–1}),¹⁴⁰ which may suggest that the CO bonding in 58 resembles that found in these supported catalysts.

The Au(III)–CO bonding was investigated by DFT methods. Significantly, none of the occupied molecular orbitals show any involvement in Au–CO π -interactions. These are prominent in the LUMO which, however, is separated from the HOMO by a large energy gap (Fig. 2). The Au–C interaction is a single bond, according to natural bond orbital analysis, with the major contributions from gold derived from the 6s, 6p_y and 5d_{x²–y²} molecular orbitals.

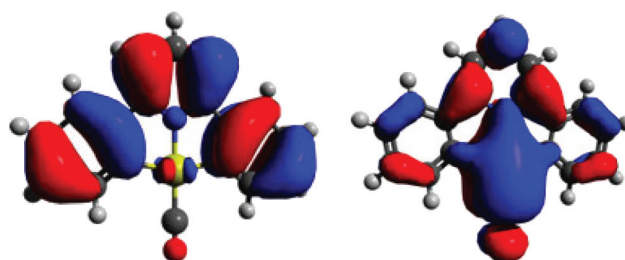
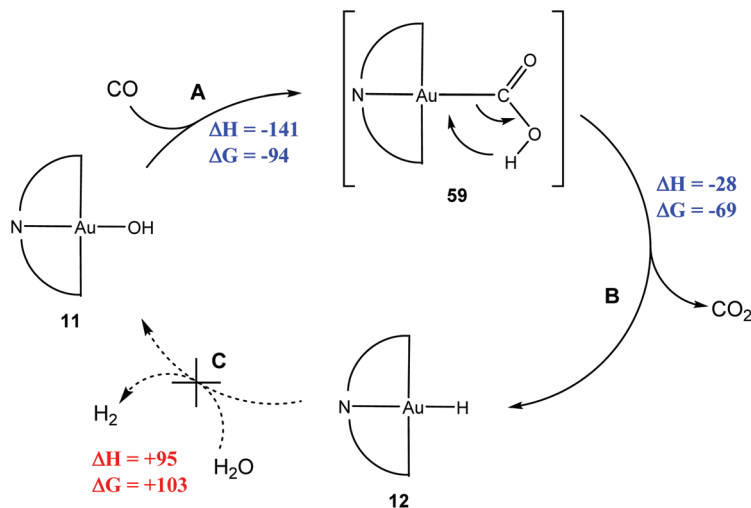


Fig. 2 HOMO (left) and LUMO (right) of [(C[^]N[^]C)Au(CO)]⁺ as simulated by DFT.

The low-temperature solution IR spectra of 58 and 58-¹³C were always accompanied by bands at 2338 cm^{–1} for ¹²CO₂ and 2273 cm^{–1} for ¹³CO₂, respectively (CH₂Cl₂). Since the CO₂ must have originated from the CO complex, this observation pointed to a gold-mediated water–gas shift reaction due to the presence of traces of moisture condensation under the recording conditions (–20 °C).

The water–gas shift (WGS) reaction (CO + H₂O → CO₂ + H₂; exothermic, $\Delta H_r = -41.2 \text{ kJ mol}^{-1}$) is catalysed by heterogeneous gold and platinum catalysts,^{145,146} with gold exhibiting a significantly lower activation energy than platinum.^{147,148} The mechanism of the heterogeneous WGS reaction is as yet poorly understood. At least three mechanisms are being discussed:¹⁴⁹ (1) the redox mechanism assumes reduction of the oxide support, which is then re-oxidised by H⁺ to generate H₂; (2) the formate mechanism assumes CO insertion into surface-bound Au–OH to give Au–OC(O)H, which then decomposes to give AuH + CO₂, and (3) in the carboxylate mechanism CO and AuOH give Au–COOH, which also decomposes to CO₂ + AuH. The nature of the catalytically active species is equally uncertain, and the debate concerns whether the active species are dispersed and mononuclear, whether they are gold nanoparticles or in fact metal ions, and if so, in which oxidation state. There are arguments in favour of nanoparticles and gold clusters,¹⁵⁰ as well for dispersed gold ions. Very recent proposals for active sites have included models such as Au(O)_x(OH)_y(Na)₉ (*e.g.* $x = 6, 7$; $y = 2$) with octahedrally coordinated gold in remarkably high oxidation states,¹⁵¹ with





Scheme 29 WGS-type reactions of (C^NC)AuOH. Enthalpy and Gibbs free energy values (in kJ mol⁻¹) for reaction steps as calculated by DFT (*T* = 298.15 K).¹⁴⁴

little apparent account of the coordination chemistry and ionisation potentials of gold.

The isolation of a well-defined Au(III)-CO complex **58** has now allowed the role of Au(III) in the WGS reaction to be explored. By contrast, for none of the well-known Au(I) and Pt(II) CO complexes has WGS activity been reported.

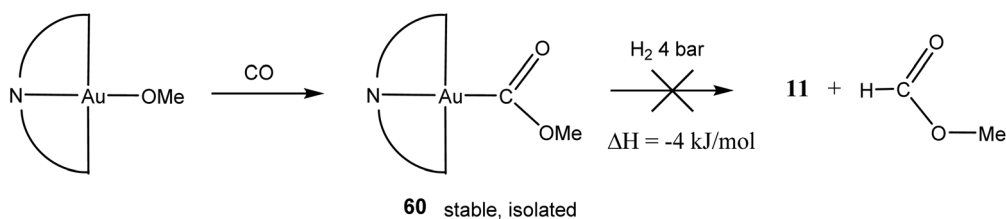
In order to monitor the reaction by NMR spectroscopy, (C^NC)AuOH (**11**) was used as a surrogate for water; in which case the WGS product would be (C^NC)Au-H (**12**) instead of H₂, which of course has an easily recognisable NMR signature.¹⁴⁴ Exposing **11** to CO did indeed generate **12**, *via* a hypothetical carboxylate intermediate (C^NC)Au-COOH (**59**) (Scheme 29). Reactions A, B and C are part of a WGS cycle according to the carboxylate mechanism. Calculations showed that overall steps A and B are 181 kJ mol⁻¹ more favourable for gold than for platinum. Once again, the high stability of the hydride **12** prevented the closure of the cycle, since it does not react with H₂O or acids to liberate H₂.

Although intermediate **59** could not be spectroscopically identified, support for its formation comes from the analogous reaction of CO with the methoxide (C^NC)AuOMe. The product, (C^NC)Au-COOMe (**60**), is thermally stable and was isolated as white crystals (Scheme 30). In an effort to explore possible formate formation as observed in heterogeneous WGS

catalysis, attempts were made to hydrogenolyse **60** under 4 bar H₂. However, methylformate was not observed; the reaction was in any case calculated to be almost thermoneutral.

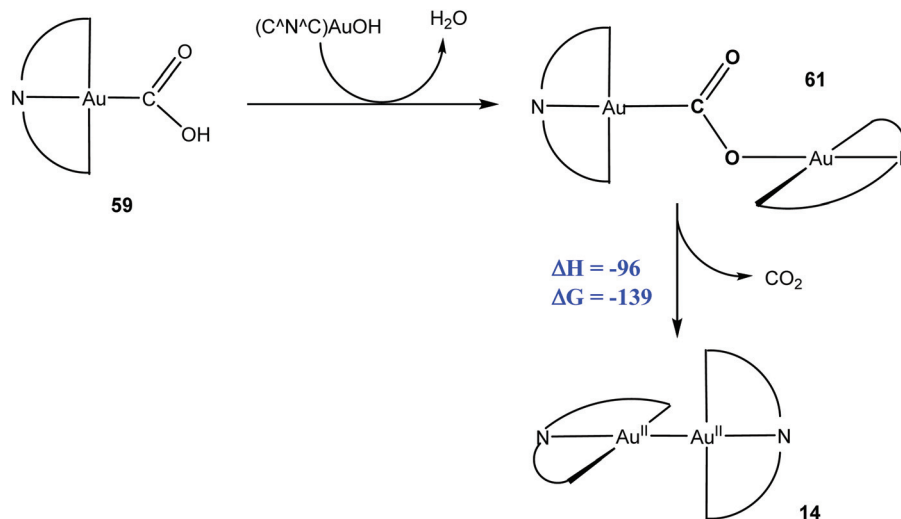
In addition, the reaction of **11** with CO also produced the CO₂-bridged complex **61**, which is most probably formed in an off-cycle reaction by condensation of intermediate **59** with excess hydroxide. Compound **61** was structurally characterised; it represents the first CO₂ complex of gold in any oxidation state. On heating to 80–120 °C, **61** was found to release CO₂ in a reductive elimination process, to give the thermally stable Au(II) complex **14** (Scheme 31).

The results show that there is a very significant difference in terms of susceptibility to nucleophilic attack between CO complexes of Au(III) and Pt(II). This is in spite of the fact that **58** and, for example, *cis*-PtCl₂(CO)₂ have very similar ν_{CO} frequencies, which could be taken to mean that the C atoms in the CO ligands should possess similar degrees of electrophilicity. Drastic differences were however revealed in the donation/back-donation ratio (d/b), as estimated by charge decomposition analysis. [(C^NC)Au(CO)]⁺ shows a d/b ratio of 2.26, compared to a value of only 0.65 for PtCl₂(CO)₂ (Scheme 32).¹¹⁹ Evidently back-donation, even for CO complexes with high frequencies, is much more prominent in Pt(II) than in Au(III). The study also demonstrates that it is the d/b

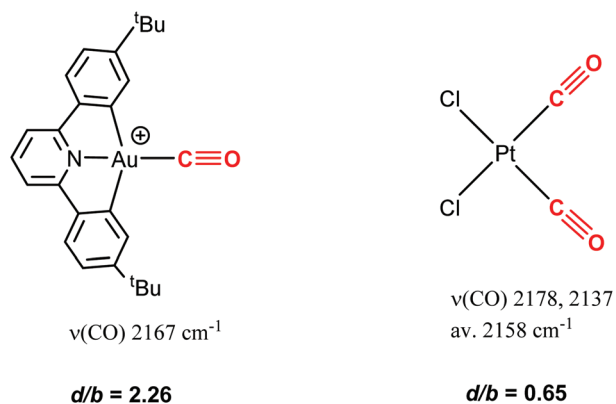


Scheme 30





Scheme 31 Thermally induced reductive CO_2 elimination from a di-gold complex. Enthalpy and Gibbs free energy values (kJ mol^{-1}) as calculated by DFT ($T = 298.15 \text{ K}$).



Scheme 32 CO stretching frequencies (Au: CH_2Cl_2 ; Pt: benzene) and donation/back-donation ratios in Au and Pt carbonyls.

ratio, rather than the IR frequency, which provides the more informative guide to chemical reactivity.

Conclusion

In summary, this Perspective has highlighted some recent advances in gold chemistry, alongside some of its peculiarities. The characteristics that set gold apart from other metals, and even from its neighbour in the Periodic Table, platinum, are the high electronegativity, with the resulting highly covalent character of the Au–H and Au–C bonds, and the order of bond strengths: Au–H > Au–C ≥ Au–O, which runs counter to experience with other transition metals. These special characteristics need to be kept in mind in mechanistic proposals for gold catalysed reactions. The last few years have also seen the isolation of some long sought-after representatives of important compound

classes; in particular, the first examples of gold(III) hydride, olefin and CO complexes. Bonding studies have highlighted the absence of π -bonding contributions to and from the metal centre, which appears to be the overriding bonding characteristic of gold(III). This applies to Au–O bonds (absence of ligand-to-metal donation) as well as to alkene and CO complexes (absence of metal-to-ligand back-bonding). In the case of CO complexes this has remarkable consequences for reactivity, and illustrates an unexpectedly drastic difference between gold and platinum.

These advances notwithstanding, many types of organo-metallic complexes that are commonplace for other d^8 metals are still missing, such as complexes with labile sites *cis* to H, CO or alkenes, also dihydrides, dicarbonyls and alkyne complexes, as well as cationic and anionic hydrides and carbonyls, hydrido and carbonyl phosphine complexes, and so forth. The synthesis of these much more reactive species will be both challenging and instructive, not least since these are the types of compounds that are likely to be realistic intermediates in catalytic cycles. The chemistry of gold can be expected to provide some intriguing surprises yet.

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