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Reactivity of Gold Complexes towards Elementary Organometallic Reactions

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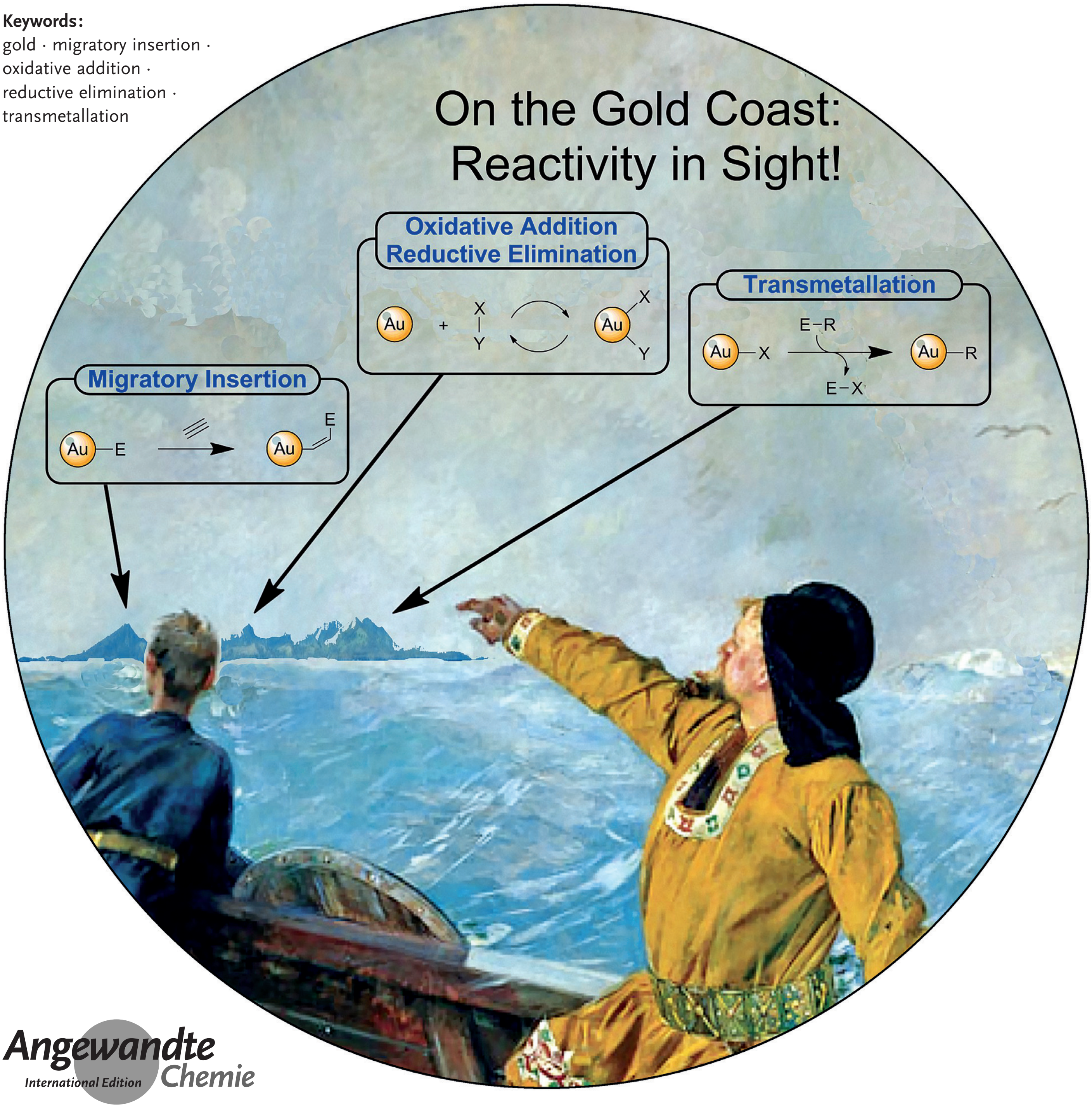

For a while, the reactivity of gold complexes was largely dominated by their Lewis acid behavior. In contrast to the other transition metals, the elementary steps of organometallic chemistry—oxidative addition, reductive elimination, transmetallation, migratory insertion—have scarcely been studied in the case of gold or even remained unprecedented until recently. However, within the last few years, the ability of gold complexes to undergo these fundamental reactions has been unambiguously demonstrated, and the reactivity of gold complexes was shown to extend well beyond π-activation. In this Review, the main achievements described in this area are presented in a historical context. Particular emphasis is set on mechanistic studies and structure determination of key intermediates. The electronic and structural parameters delineating the reactivity of gold complexes are discussed, as well as the remaining challenges.

From the Contents

1. Introduction

The use of gold complexes in homogeneous catalysis is a fascinating story full of unforeseen developments. For a while, gold complexes were considered as inert and stigmatized as "catalytically dead" species.[1] This view changed in the late 1990s when the carbophilic properties of gold complexes were discovered,[1,2] making them valuable catalysts for the activation and functionalization of π-C–C bonds.[3,4] From that time, the use of gold complexes in catalysis has developed very rapidly and broadly, and within less than two decades, gold catalysis has emerged as a very efficient method in organic synthesis, enabling the rapid construction of complex and highly functionalized molecules.[5]

In parallel with these synthetic achievements, renewed interest has been devoted to the fundamental behavior of gold complexes that had been almost ignored after a few pioneering contributions back in the 1970s. Several key intermediates have now been characterized and new types of complexes have been discovered,[6–9] but the manifold of reactivity patterns known for gold complexes still remains very limited compared to that of the other transition metals. Until recently, several elementary steps of organometallic chemistry were still considered highly disfavored, if not impossible, for gold complexes. However, this situation noticeably changed within the last few years and significant progress has been achieved. Several groups have started to investigate the reactivity of gold complexes with the following guiding question: is it possible to extend the reactivity of gold beyond π-activation? In other words, can gold complexes undergo the elementary steps that compose most catalytic cycles, that is, oxidative addition, reductive elimination, transmetallation, and migratory insertion?

Over the past five years, the ability of gold complexes to undergo these elementary reactions has been evidenced, and first insights have been gained in the underlying factors. It is the purpose of this Review to discuss these recent achievements within their historical context and to highlight the fact that the reactivity of gold complexes is actually much more versatile than anticipated. The focus is set on contributions dealing with well-defined species and providing mechanistic insights by experimental (kinetic studies, characterization/isolation of reactive intermediates, stoichiometric studies) and/or computational methods (DFT calculations, reaction profiles). The Review is built up so as to highlight the key factors governing the reactivity of gold complexes for each type of elementary transformation. We hope it will represent a valuable basis to deepen our knowledge of gold reactivity and to further expand its scope. The Review is also intended to stimulate the development of new gold-mediated transformations based on new reactivity patterns of gold complexes.

2. Oxidative Addition

Oxidative addition, a key elementary step in transition-metal chemistry, is the entry point to many catalytic transformations, in particular cross-coupling reactions. The ability of transition metals to promote the oxidative addition of a large set of polar and apolar σ-bonds is well established and the associated mechanisms are well understood, especially for late transition metals.[10] In striking contrast, this elementary reaction remained for a long time elusive in gold chemistry. Despite the availability and stability of +I, +II, and +III oxidation states, gold complexes are often considered as

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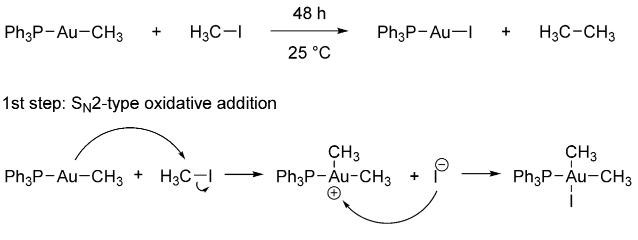
redox-neutral catalysts and Au^{I}/Au^{III} cycles are very rarely encountered. To date, catalytic cross-coupling reactions mediated by gold complexes require the use of stoichiometric amounts of strong external oxidants (usually I^{III} derivatives, X_2 or other X^+ sources, X = halogen) to promote $Au^{I} \rightarrow Au^{III}$ oxidations.[11,12] While ubiquitous with palladium, oxidative addition was until recently considered to be highly disfavored, if not impossible with gold.[13–15] The reluctance of gold(I) complexes to undergo oxidative addition is commonly attributed to the high redox potential of the Au^{I}/Au^{III} couple compared to that of the isolelectronic Pd^{0}/Pd^{II} couple.[16]

However, recent studies have shown that other factors, electronic and structural features in particular, can play a major role in the reactivity of gold(I) complexes.[17] Fundamental organometallic investigations have indeed substantiated the ability of gold(I) complexes to undergo oxidative addition of $C(sp^3)-X$ bonds, $C(sp^2)-X$ bonds, as well as apolar σ-bonds (Si–Si, Sn–Sn, and even C–C). These achievements are presented in this Section and the key properties of the corresponding gold complexes (coordination number, geometry) are discussed.

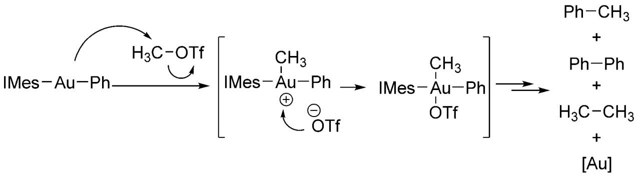
2.1. *Oxidative Addition to Linear Two-Coordinate Gold(I) Complexes*

The reactivity of two-coordinate linear gold(I) complexes towards oxidative addition was investigated early on. Kochi, Puddephatt, and Schmidbaur discovered in the 1970s that phosphine gold(I) methyl complexes react slowly but quantitatively with methyl iodide to give ethane and phosphine gold(I) iodide (Scheme 1).[18–20] The reaction sequence starts by oxidative addition of the $C(sp^3)-I$ bond to gold, for which an S_N2-type mechanism, akin to that generally observed with late transition metals,[9] was suggested. In some cases, the resulting gold(III) complexes have been spectroscopically characterized. The release of ethane is not a simple reductive elimination, but follows a rather unusual two-step mechanism involving a CH_3–I transmetallation between the intermediate dimethylgold(III) iodide complex and the starting methylgold(I) complex.



Scheme 1. Reaction of a phosphine gold(I) methyl complex with methyl iodide.

More recently, Wendt and Ahlquist drew similar conclusions for an N-heterocyclic carbene (NHC) gold(I) aryl complex. Indeed, (IMes)Au-Ph (IMes = (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)) reacts with methyl iodide at 110 °C and with methyl triflate at room temperature to yield mixtures of C–C coupling products, that is, toluene, biphenyl, and ethane (Scheme 2).[21] No gold(III) intermediate could be detected, but the feasibility of $C(sp^3)$–OTf oxidative addition to gold(I) (via an S_N2-type mechanism) and of subsequent C–C couplings was supported by DFT calculations.



Scheme 2. Reaction of (IMes)AuPh with MeOTf giving rise to C–C coupling products.

Toste and Levin reported the cross-coupling of allyl bromides and arylboronic acids with gold complexes (Scheme 3).[22] Thorough studies have been performed to shed light on the mechanism of this transformation, and in particular phosphine gold(I) aryl complexes were unambiguously shown to promote the oxidative addition of $C(sp^3)-Br$ bonds.

Stoichiometric reactions support a mechanism different from that usually encountered with Pd. Transmetallation from boron to gold would occur first and the resulting gold aryl complex would then undergo oxidative addition of the allyl bromide. The dinuclear complex deriving from the bis(phos-

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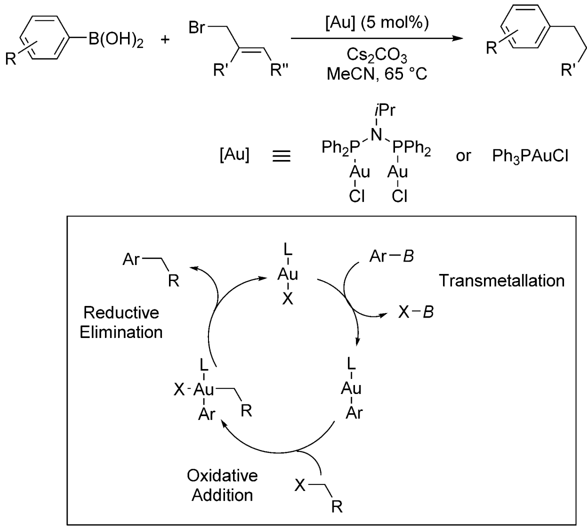
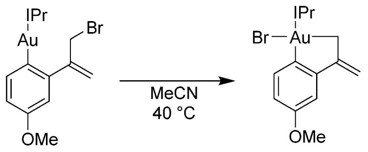
Abderrahmane Amgoune received his PhD in 2006 at the University of Rennes (Profs. J.-F. Carpentier and C. Thomas). He then moved to the University of Konstanz as an Alexander-von-Humboldt postdoctoral research associate with Prof. S. Mecking. In 2008, he was appointed a CNRS research position at the University of Toulouse. His current research interests are in coinage metal chemistry, gold in particular (coordination chemistry and reactivity), and involves rational design of metal complexes for the development of new catalytic reactions for organic synthesis and polymer materials.



Scheme 3. Gold-catalyzed C(sp^3)–C(sp^2) cross-coupling. Inset: simplified catalytic cycle (with transmetalation first)

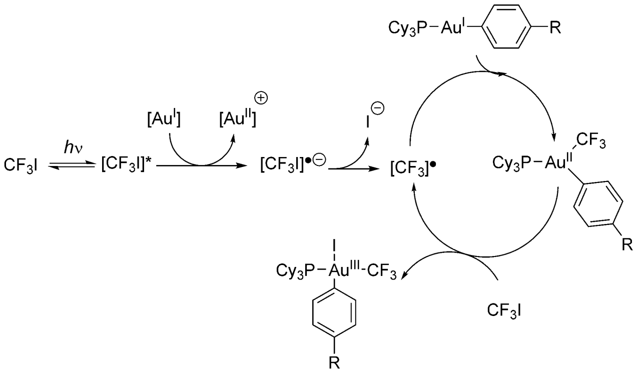
phine) ligand iPrN(PPh$_2$)$_2$ proved to be considerably more active than simple (R$_3$P)AuCl complexes. Although this effect has not been clearly assessed, it is consistent with the proximity of the two metal centers that may facilitate the C(sp^3)–Br oxidative addition.[23,24] The intermediate gold(III) species was not characterized in intermolecular reactions, probably because of fast C–C coupling, but a gold(I) aryl complex featuring a tethered allyl bromide moiety enabled to substantiate the process in intramolecular conditions (Scheme 4).



Scheme 4. Intramolecular oxidative addition of an allyl bromide to a two-coordinate NHC-Au-aryl complex.

Maximilian Joost obtained his BSc from the University of Heidelberg, Germany and then moved to France where he completed his MSc (with Dr. S. Sabo-Etienne and Dr. G. Alcaraz) in 2011 at the University Paul Sabatier, Toulouse. He subsequently obtained a PhD (2014), from the same university, under the supervision of Dr. D. Bourissou and Dr. A. Amgoune. His PhD studies revolved around new aspects of the coordination chemistry of the coinage metals. He is at present a post-doctoral fellow with Prof. Dr. K. Lammertsma and Dr. Chris Slootweg (VU Amsterdam); his current research concerns organometallic and phosphorus chemistry.

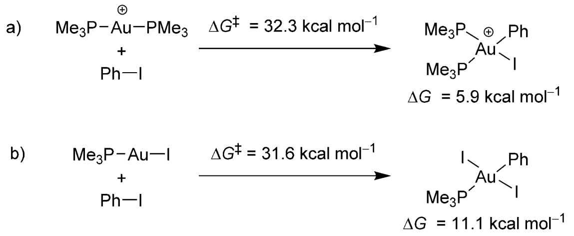
Recently, two-coordinate phosphine gold(I) aryl complexes were shown to react with CF$_3$I under near-ultraviolet irradiation.[25] The ensuing gold(III) complexes are remarkably stable and were characterized by X-ray diffraction studies. Mechanistic studies point towards a photoinitiated radical chain reaction (Scheme 5). First, photoexcited CF$_3$I would be reduced by the gold(I) aryl complex and the ensuing radical anion [CF$_3$I]$^{\bullet-}$ would split into iodide and [CF$_3$]$^\bullet$. Then, propagation would involve two steps: addition of [CF$_3$]$^\bullet$ to [(Cy$_3$P)Au(Ar)] to give a tricoordinate gold(II) complex, followed by oxidation by CF$_3$I to yield the trifluoromethyl aryl gold(III) complex.



Scheme 5. Radical chain mechanism proposed for the formal oxidative addition of CF$_3$I to two-coordinate phosphine gold(I) aryl complexes (R = H, F, Me, OMe).

From these contributions, linear two-coordinate organogold(I) complexes LAuR (L = NHC or phosphine, R = Me or Ph) appear capable and actually quite prone to activate C(sp^3)–X bonds. These formal oxidative additions occur under mild conditions and proceed via S$_N$2-type or radical mechanisms.

A significant interest was also devoted to the activation of aryl halides at gold. In the course of the investigations of heterogeneous gold-catalyzed cross-coupling reactions of aryl iodides with arylboronic acids or phenylacetylenes,[26,27] Corma and co-workers proposed in 2007 that linear two-coordinate gold(I) complexes may be good candidates for the Sonogashira coupling reaction. These results raised an intense debate,[28] and several mechanistic investigations were then performed to establish the nature of the active species, in particular for the oxidative addition of the aryl iodide. Corma's group confirmed the intrinsic activity of gold by kinetic studies in the presence of known amounts of Pd impurities and performed calculations on the activation of iodobenzene at gold.[29] Oxidative addition to (Me$_3$P)AuI was predicted to be endothermic and to involve a very high activation barrier (Scheme 6). In contrast, activation of PhI across an edge of a Au$_{38}$ nanoparticle was found to be thermodynamically favored and kinetically facile, suggesting that the presence and cooperativity of several metal centers play a major role. It was concluded that small gold clusters/nanoparticles formed in situ by decomposition of the gold(I)



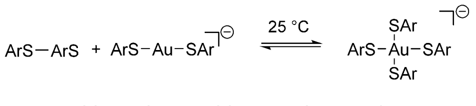
Scheme 6. Activation barriers and reaction energies computed for the oxidative addition of PhI to linear two-coordinate gold(I) complexes.

complexes are most likely the active species in these cross-coupling reactions.[30]

By combining mass-spectrometry experiments and DFT calculations, O'Hair and co-workers soon after corroborated the key influence of nuclearity of the gold species on the activation of idodobenzene. In contrast to small gold clusters, such as $[Au_3(diphosphine)]^+$, two-coordinate mononuclear complexes $[(R_3P)_2Au]^+$ (R = Me, Ph) were found to be highly stable and not to react with iodobenzene in the gas phase.[31] According to DFT calculations, the product lies uphill in energy and the activation barrier for this reaction is very high (Scheme 6). The activation of iodobenzene by an NHC gold(I) complex has also been investigated by Ahlquist, Wendt and co-workers. Upon heating at 110 °C for 50 h, biphenyl was obtained quantitatively,[21] but DFT calculations indicated a very high barrier for oxidative addition of PhI to (IMes)Au-Ph ($\Delta G^{\neq}$ 40.4 kcal mol^{-1}).

Thus, the activation of C(sp^2)–X bonds at gold seems limited to polymetallic species (clusters, nanoparticles, surfaces) and oxidative addition of aryl halides to linear two-coordinate gold(I) complexes is highly disfavored. To favor the process, it was appealing to take advantage of chelating assistance and to envision intramolecular reactions. As described in the next Section, this strategy proved successful and made it possible to substantiate the feasibility of oxidative addition to mononuclear gold(I) complexes.

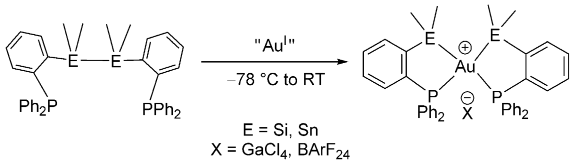
Note at this stage that the inert character of linear two-coordinate gold(I) complexes towards oxidative addition finds a noticeable exception. Bachman et al. reported in 2008 the oxidative addition of activated disulfides $[Ar^FSSAr^F]$ to electron-rich dithiolate aurate species $[(Ar^FS)Au(SAr^F)]^-$ ($Ar^F = C_6F_5$ or p-C_6F_4H; Scheme 7).[32,33] Both the gold(I) and the gold(III) thiolate complexes were structurally characterized, and the reversibility of the process was demonstrated.



Scheme 7. Reversible oxidative addition/reductive elimination of activated disulfides at gold ($Ar_F = C_6F_5$, p-C_6F_4H).

2.2. Intramolecular Oxidative Addition with Two-Coordinate Complexes

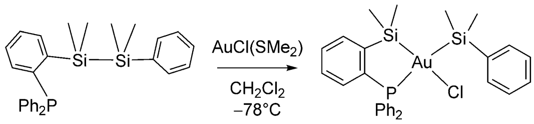
Diphosphine ligands tethering Si–Si, Sn–Sn, or C(sp^2)–X bonds were designed by Amgoune and Bourissou with the aim to position the σ-bond to be activated close to the metal center and thereby provide favorable conditions to form and stabilize the oxidative addition complexes. Upon coordination of $[R_2P(o\text{-}C_6H_4)Me_2E\text{-}EMe_2(o\text{-}C_6H_4)PR_2]$ (E = Si, Sn, R = Ph, iPr) to gold(I), spontaneous oxidative addition of the Si–Si[34,35] and Sn–Sn[36] bonds was observed (Scheme 8).[37]



Scheme 8. Formation of bis(silyl)- and bis(stannyl) gold(III) complexes by chelation-assisted oxidative addition of Si–Si or Sn–Sn bonds to gold(I). $BArF_{24}^-$ = tetrakis[bis(3,5-trifluoromethyl)phenyl]borate.

The reactions proceed readily at low temperature (−78 °C), without detectable intermediates. The ensuing cationic bis(silyl) and bis(stannyl) gold(III) complexes can be isolated as stable solids. They have been fully characterized by multinuclear NMR spectroscopy and X-ray diffraction (they adopt square-planar *cis* geometries).

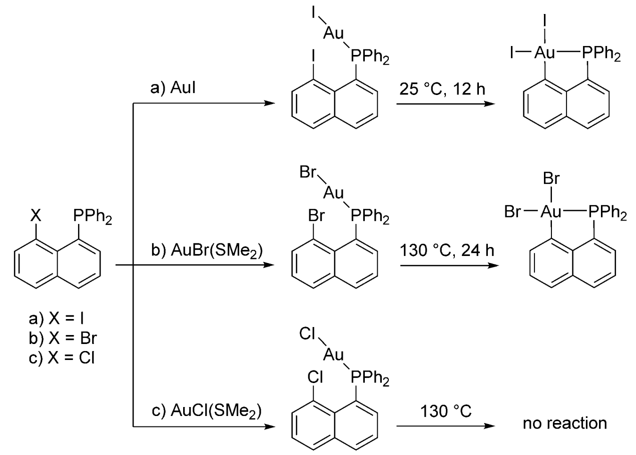
Interestingly, spontaneous intramolecular oxidative addition of the Si–Si bond to gold(I) was observed even when the Si–Si bond was supported by only one phosphine donor arm (Scheme 9).[34]



Scheme 9. Spontaneous oxidative addition of a Si–Si bond tethered by a single phosphine buttress to gold.

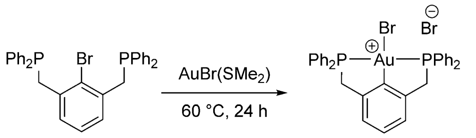
Amgoune, Bourissou, and co-workers then took advantage of phosphine-chelation assistance to investigate the oxidative addition of aryl halides, with the aim to provide the first direct evidence for the C(sp^2)–X oxidative addition to a gold(I) center.[38] 8-Halonaphthyl phosphines were selected as suitable ligands to position the C(sp^2)–X bond in close proximity to the gold center upon coordination of the phosphine (Scheme 10). Intramolecular oxidative addition of the C(sp^2)–I bond was shown to readily occur at room temperature to give a stable P,C-cyclometallated gold(III) diiodo complex.

The reaction was shown to follow first-order kinetics, in line with an intramolecular unimolecular process. The activation barrier determined by NMR ($\Delta G^{\neq} = 21 \pm 7$ kcal mol^{-1} at 25 °C and $\Delta H^{\neq} = 25 \pm 4$ kcal mol^{-1}) was well reproduced computationally. It is 10–15 kcal mol^{-1} lower than that



Scheme 10. Coordination of 8-halo naphthyl phosphines to gold(I) followed by intramolecular $C(sp^2)-I$ and $C(sp^2)-Br$ oxidative addition.

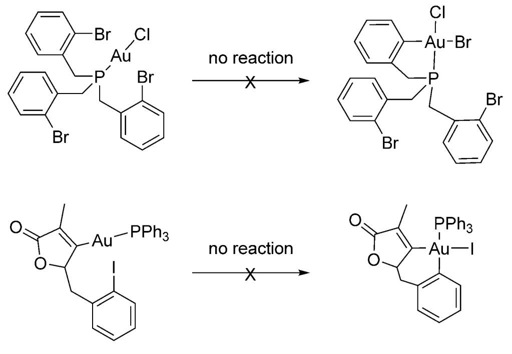
predicted for related intermolecular reactions, oxidative addition of PhI to two-coordinate gold(I) complexes. The activation of the corresponding $C(sp^2)-Br$ bond requires heating at 130 °C to proceed, while oxidative addition of the $C(sp^2)-Cl$ bond was not observed even at elevated temperatures. These phosphine-directed $C(sp^2)-X$ oxidative additions give access to original P,C-cyclometallated gold(III) complexes. Activation of the $C(sp^2)-Br$ proceeds under milder conditions when the aryl bromide bears two phosphine buttresses, resulting in the clean formation of a PCP-pincer gold(III) complex (Scheme 11).[38] According to DFT calculations, the reaction proceeds through bidentate coordination of phosphines to gold, followed by facile intramolecular $C(sp^2)-Br$ oxidative addition ($\Delta G^{\neq} = 16.3\ \mathrm{kcal\,mol^{-1}}$).



Scheme 11. Synthesis of a PCP-pincer gold(III) complex via $C(sp^2)-Br$ oxidative addition.

The importance of the second phosphine arm for the oxidative addition of the $C(sp^2)-Br$ bond was corroborated by a report from Echavarren and Maseras and co-workers.[39] Monodentate tris(2-bromobenzyl)phosphine gold(I) chloride does not undergo intramolecular oxidative addition of the pendant $C(sp^2)-Br$ bond, even after prolonged heating (Scheme 12). Calculations indicate that the oxidative addition is precluded due to a high-lying transition state (ca. 45 kcal mol^{-1}). Note also that a phosphine vinylgold(I) complex bearing an aryl iodide moiety was shown by Hashmi et al. to be stable, and not to undergo intramolecular $C(sp^2)-I$ oxidative addition (Scheme 12).[15]

The chelating-assistance strategy enabled the oxidative addition of E–E (Si, Sn) and $C(sp^2)-X$ (X = I, Br) bonds to dicoordinate gold complexes to be confirmed. The coordination of the phosphine buttresses favors the oxidative addition entropically and enhances the stability of the resulting gold(III) complexes. It is clear that the bifunctional character and rigidity of the ligand play an important role and this naturally raises the question of the feasibility of related intermolecular transformations.



Scheme 12. $C(sp^2)-Br$ and $C(sp^2)-I$ bonds in close proximity to a gold(I) center which do not undergo oxidative addition.

Neutral and cationic dicoordinate complexes LAuX (X = halogen, alkyl, or aryl) and $[L_2Au]^+$ are reluctant to coordinate and activate σ-bonds. This reluctance has been associated to the high deformation energy required to go from a stable linear two-coordinate geometry to a bent fragment in a three-coordinate gold complex.[40] To trigger the reactivity of gold(I) and achieve intermolecular oxidative addition, two strategies have been explored. The first relies on the generation of highly electron-deficient monocoordinate gold species $[LAu]^+$ (formally 12 e^- complexes, usually stabilized by a weakly coordinating anion). The second strategy is based on the design of two-coordinate gold(I) complexes with bent geometry to reduce the deformation energy required for the activation process.

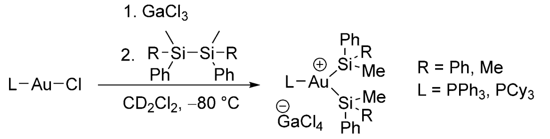
2.3. Oxidative Addition to Monocoordinate Gold(I) Complexes

In the course of gas-phase studies, O'Hair and co-workers explored the reaction of phosphine gold(I) cations $[(R_3P)Au]^+$ (R = Me, Ph) with iodobenzene.[31] Mass spectrometry analyses indicated the formation of $[(R_3P)Au(PhI)]^+$ adducts that subsequently fragmented into phenyl phosphonium cations (P–Ph bond formation) and presumably gold iodide (Scheme 13). The overall process may be explained by an oxidative addition/reductive elimination sequence via a gold(III) species. DFT calculations indeed suggested an accessible activation barrier ($\Delta E^{\neq} = 24.7\ \mathrm{kcal\,mol^{-1}}$) for the oxidative addition starting from the $[(Me_3P)Au(PhI)]^+$

Scheme 13. Gas-phase reaction of a phosphine gold(I) cation with phenyl iodide, as studied by mass spectrometry.

adduct. The subsequent reductive elimination from the gold(III) intermediate was found to be a very facile exothermic process.

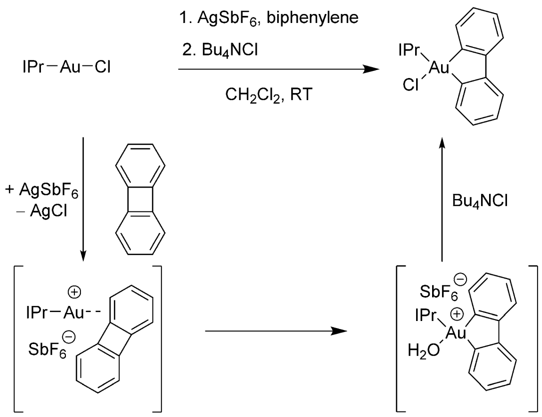
As an extension of the work on the intramolecular oxidative addition of σ-Si–Si bonds, Amgoune, Bourissou, and co-workers recently explored the behavior of phosphine gold(I) complexes towards disilanes. No reaction occurred with two-coordinate phosphine gold(I) chlorides, but cationic complexes generated upon addition of $GaCl_3$ readily undergo oxidative addition at −80 °C (Scheme 14).[41]



Scheme 14. Synthesis of bis(silyl) gold(III) complexes via intermolecular oxidative addition of disilanes.

The resulting bis(silyl) gold(III) complexes are highly unstable, and they were characterized by multinuclear NMR spectroscopy at low temperature. According to DFT calculations performed by Maron and Miqueu, the Si–Si bond activation proceeds in one-step with a low activation barrier from the tight ion pair $[(Ph_3P)Au]^+[GaCl_4]^-$ ($\Delta H^{\neq} = 11.7\ \mathrm{kcal\,mol^{-1}}$) and the tricoordinate gold(III) bis(silyl) complexes adopt distorted Y-shaped geometry.

Toste and co-workers reported very recently the oxidative addition of strained C–C bonds (biphenylenes) to coordinatively unsaturated NHC-gold(I) cationic complexes.[17,42] The reactions proceed under very mild conditions in contrast to the relatively harsh conditions often required for other late transition metals.[43,44] Typically, the reaction of biphenylene with (IPr)AuCl in the presence of $AgSbF_6$ immediately afforded the [(IPr)Au(biphenylene)]$^+$ adduct, and C–C bond activation then occurred within 1.5 h at room temperature. The resulting cationic gold(III) complex was trapped with ammonium chloride to generate the more stable tetracoordinate chloro gold(III) complex (Scheme 15). The cationic gold(III) complex proved to be a very efficient catalyst for Michael additions, [4+2] and [2+2] cycloadditions to α,β-unsaturated carbonyl compounds.



Scheme 15. Synthesis of stable gold(III) complexes via oxidative addition of strained C–C bonds to NHC-gold(I) cationic complexes.

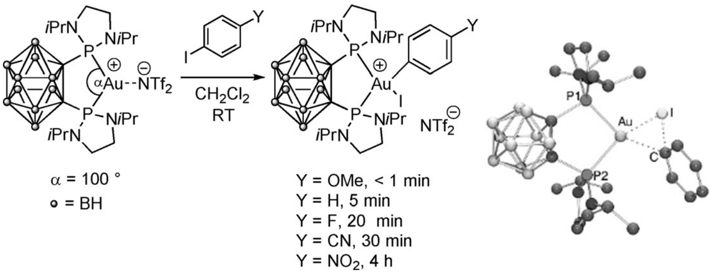
These results demonstrate the ability of monocoordinate cationic gold(I) complexes to undergo intermolecular oxidative additions. The three-coordinate gold(III) complexes resulting from C(sp^2)–I and Si–Si activation are too unstable to be isolated. Oxidative addition of biphenylene gives relatively stable cyclometallated complexes, which are highly reactive and open new perspectives in Lewis acid catalysis.

2.4. Oxidative Addition to Bent Two-Coordinate Gold(I) Complexes

A different strategy to trigger oxidative addition to gold(I) is based on the design of cationic two-coordinate bent complexes using bidentate ligands with small bite angles. The bending of two-coordinate ML_2 fragments is known to enhance the reactivity of Pd (and all Group 10 metals) towards oxidative addition.[45] Bent L-M-L fragments are preorganized to accommodate the square-planar geometry of the oxidative addition products. Bending also influences the energy level and hybridization of the key frontier orbitals (in particular the HOMO is raised in energy and displays suitable symmetry to interact with the σ* orbital of the bond to be activated).[46]

This bending approach had not been applied to gold until very recently, mainly because of the strong preference of gold for two-coordinate linear geometry and its high tendency to engage in aurophilic interactions.[3c,13,47,48] Accordingly, most bidentate ligands known to chelate Group 10 metals form dinuclear structures with gold(I).[49] Carborane diphosphines (DPCb) are in fact among the rare ligands known to chelate gold(I) with small PAuP bite angles (90–100°),[50] offering the opportunity to explore the influence of bending on the reactivity of gold. Using tricoordinate (DPCb) complexes with a labile triflimidate ligand (NTf_2^-), Amgoune, Bourissou, and co-workers demonstrated the ability of gold(I) to undergo oxidative addition of aryl iodides (Scheme 16).[17,51] The reaction proceeds under mild conditions (minutes to hours at −30 °C to RT) and is broad in scope.[52] The ensuing aryl gold(III) complexes have been isolated and fully characterized (NMR spectroscopy, X-ray diffraction). Interestingly, the reactivity trend observed for *p*-substituted iodobenzenes is opposite to that usually encountered with Pd^0 complexes. With (DPCb) gold complexes, electron-rich substrates react faster than electron-poor ones.

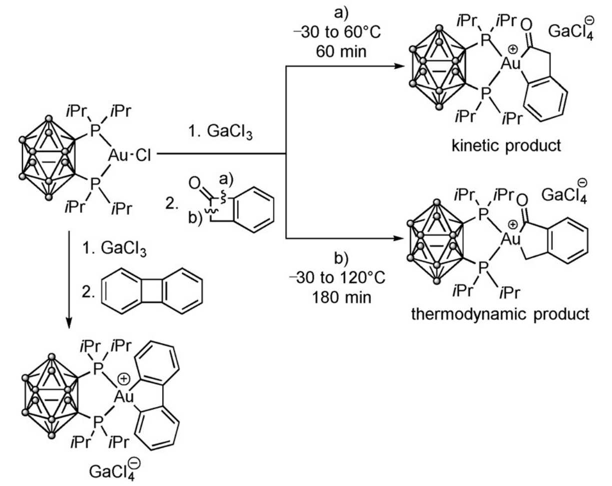
According to DFT studies by Miqueu, the reaction involves displacement of the weakly coordinating NTf_2 counteranion by the aryl iodide (giving a π-complex) followed by concerted oxidative addition via a three-center transition state (Scheme 16, right). The activation barrier is remarkably low ($\Delta E^{\neq} = 10.7\ \mathrm{kcal\,mol^{-1}}$) and the prominent role of bending was substantiated by strain-activation model analyses. Indeed, the [(DPCb)Au]$^+$ fragment required very little energy to reach the TS geometry, only about 6 $\mathrm{kcal\,mol^{-1}}$ versus greater than 24 $\mathrm{kcal\,mol^{-1}}$ for the linear $[(Me_3P)_2Au]^+$



Scheme 16. Left: Oxidative addition of aryl iodides to bent gold(I) complexes. Under the aryl iodides are indicated the reaction times required to reach complete conversion into gold(III) using 5 equiv. of ArI. Right: Transition state computed for the oxidative addition of PhI.

complex. In a parallel study, Fernandez and Bickelhaupt explored computationally the factors governing oxidative addition of C(sp^2)−X bonds to gold(I) and pointed out the importance of the distortion energy of the gold fragment within the activation barrier.[53]

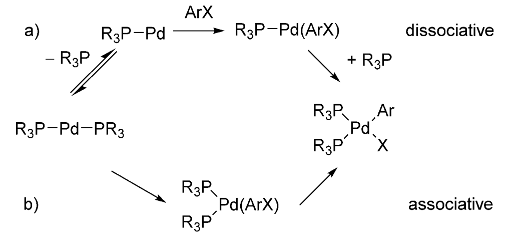
Furthermore, Amgoune, Bourissou, and co-workers found that bent [(DPCb)Au]$^+$ complexes promote the oxidative addition of strained C−C bonds of biphenylene and benzocyclobutenone (Scheme 17).[17,54] The resulting gold(III) complexes are remarkably stable (four-coordinate square-planar complexes). A peculiar selectivity is observed in the activation of benzocyclobutenone: oxidative addition can be achieved selectively at the C(aryl)−C(O) or the C(alkyl)−C(O) bond as the result of kinetic/thermodynamic control.



Scheme 17. Oxidative addition of strained C−C bonds to the bent two-coordinate complex [(DCPb)Au]$^+$

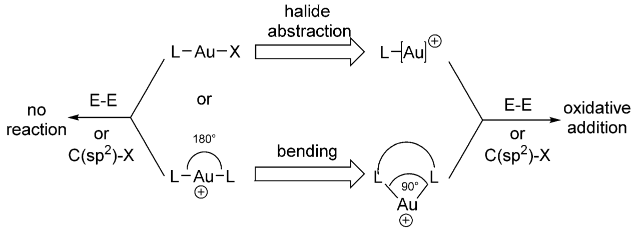
*2.4.1. **Comparison Between Gold and Palladium***

The results reported over the last few years clearly demonstrate that gold(I) complexes can undergo oxidative additions and also show that the factors governing the reactivity of Au^I are very different from those controlling the reactivity of analogous Pd^0 complexes. Two-coordinate Pd^0 species L$_2$Pd^0 (L = R$_3$P, NHC …) readily undergo oxidative addition of aryl halides and two general mechanistic pathways can be distinguished: a) dissociation of one L ligand, coordination of the Ar−X substrate to the monocoordinate LPd^0 complex, concerted oxidative addition and re-coordination of the L ligand or b) direct coordination of the Ar−X substrate to the L$_2$Pd^0 complex with bending of the L-Pd-L angle, followed by concerted oxidative addition (Scheme 18).



Scheme 18. General mechanistic pathways for the oxidative addition of aryl halides to two-coordinate Pd^0 complexes.

This mechanistic picture is hardly transposable to gold(I) complexes and this probably contributes to the reluctance of classical [L$_2$Au]$^+$ or LAuX complexes to achieve oxidative additions. Indeed, owing to the relativistic effects,[55] ligand dissociation from two-coordinate [L$_2$Au]$^+$ and LAuX complexes is highly disfavored,[56] and these linear gold(I) complexes are also reluctant to coordinate a third ligand,[40,57] because the associated deformation energy is very high.[40,53] The specific properties of gold thus require to modify its coordination sphere. The two complementary approaches based on cationic monocoordinate complexes [LAu]$^+$ and bent di-coordinate complexes [L$_2$Au]$^+$ proved successful (Scheme 19).



Scheme 19. Schematic representation of the two main approaches developed to generate reactive gold(I) complexes for oxidative addition.

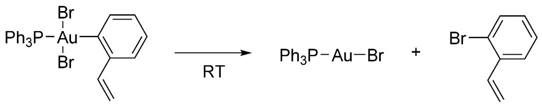
It is important to emphasize here the critical role of the ligands, which enable the intrinsic properties of gold to be overridden and to stimulate its reactivity. Another aspect to consider is the possible involvement of one-electron pathways, taking into account the photosensitive character of many gold complexes and the relative stability of Au^{II} species.

3. Reductive Elimination

Reductive elimination is the microscopic reverse of oxidative addition. It plays a major role in transition-metal-catalyzed reactions (cross-couplings in particular) as the key product-releasing step. In contrast to oxidative addition, the feasibility of reductive elimination at gold has never been questioned and it was demonstrated experimentally early on. Nevertheless, our knowledge on reductive elimination at gold remains rather limited (especially when compared with the Group 10 metals). Significant mechanistic insights have only started to be gained over the past few years, thanks to the generation of well-defined organogold(III) complexes. In this Section, historical and recent mechanistic studies on C−X and C−C reductive eliminations are presented. The key factors influencing the transformation are discussed, and the three- versus four-coordinate character of the gold(III) complexes undergoing reductive elimination is emphasized.

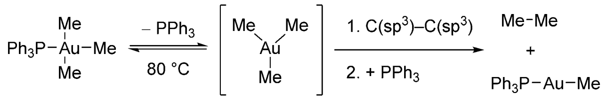
3.1. Early Studies on Reductive Elimination Processes from Gold(III) Complexes

Brain and Gibson noticed the instability of organogold(III) derivatives as early as 1939.[58] The dimethylgold(III)iodide complex, a solid which was isolated as an I-bridged dimer, was found to decompose in benzene solution at room temperature and to melt at 78 °C to a dark red liquid that violently detonates, most probably owing to the elimination of ethane. Several decades later, in 1973, Aresta and Vasapollo reported a C(sp^2)−Br bond formation upon decomposition of a phosphine dibromogold(III) aryl complex at room temperature (Scheme 20). The gold(III) species was generated by low-temperature oxidation of (Ph_3P)Au-Ar with Br_2.[59,60]



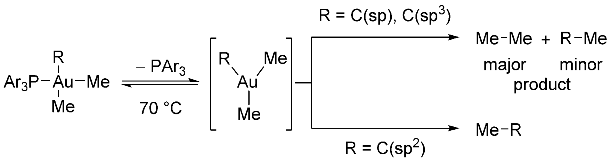
Scheme 20. C(sp^2)−Br bond-formation by reductive elimination of a dibromo(aryl)gold(III) complex.

Shortly after, the group of Kochi[61–63] reported seminal mechanistic studies on the thermal decomposition of a series of tetracoordinate alkyl gold(III) complexes, such as (Ph_3P)$AuMe_3$[62] and *cis*-$AuMe_2X(PPh_3)$[63] complexes (X = OTf, Cl, NO_3, CH_3CO_2), which readily undergo reductive elimination of ethane above 70 °C. Kinetic studies indicated significant inhibition of this decomposition process by addition of even only small amounts of phosphine. The decomposition was suggested to occur via dissociation of the phosphine as the rate-limiting step, followed by fast reductive elimination from a three-coordinate gold(III) species (Scheme 21).[64] However, the putative three-coordinate gold(III) complex was not characterized, and clear establishment of the mechanism was not possible owing to side reactions. The same dissociative pathway was proposed by Tobias and Kuch for the reductive elimination of ethane from four-coordinate cationic [*cis*-$AuMe_2(PR_3)_2]^+X^-$ (X = BF_4, PF_6, F_3CSO_3) complexes, though elimination occurs at a faster rate than for neutral gold(III) complexes.[65]



Scheme 21. Proposed mechanism for ethane elimination from (PPh_3)$AuMe_3$.

Later on, Komiya et al. investigated the selectivity of C−C bond reductive elimination from a series of (Ar_3P)$AuMe_2R$ complexes (R = alkyl, alkenyl, alkynyl, aryl).[66,67] Upon heating, different coupling products were observed depending on the hybridization of the carbon atom bound to gold (Scheme 22). For sp^3 and sp carbon moieties (R = alkyl or alkynyl), ethane was formed as the major product along with minor Me–R cross-coupling products. For sp^2 carbon atoms (R = aryl, alkenyl), the reaction yielded selectively Me–C(sp^2) coupling products. In line with a dissociative mechanism, it was also shown that less-coordinating phosphines (bearing sterically hindered or electron-withdrawing substituents) enhance the rate of Me–aryl reductive elimination.



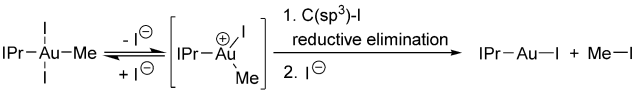
Scheme 22. C−C bond formation by reductive elimination from (organo)dimethylgold(III) complexes.

Overall, these early studies provided first insight into the reductive elimination of C(sp^3)−C(sp^3) and C(sp^3)−C(sp^2) bonds from gold(III) complexes. Two decades later, the mechanism of this elementary step was re-investigated experimentally and computationally with several types of gold complexes. Significant progress has been realized concerning the mechanism and scope of the reaction. Reductive eliminations from tricoordinate as well as tetracoordinate gold complexes have been reported and the range of coupling products has also been progressively expanded.

3.2. Reductive Elimination from Tricoordinate Gold(III) Complexes

3.2.1. C(sp^3)−X Bond Formation

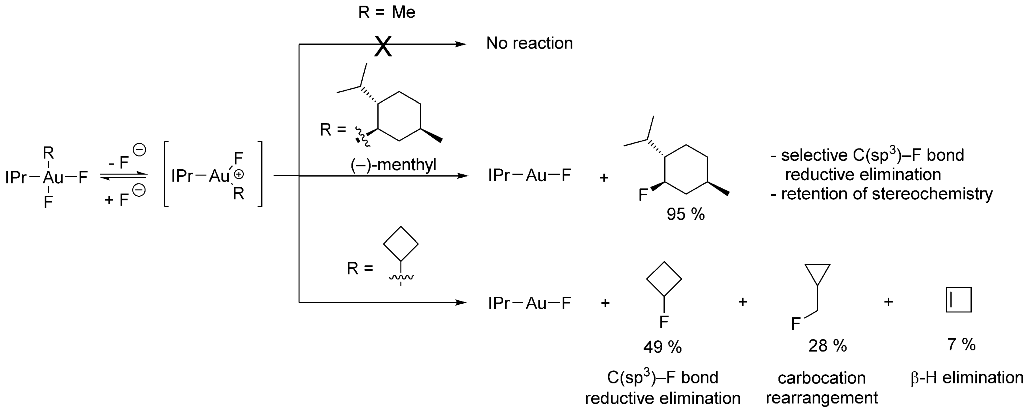
The reactivity of organogold(III) complexes supported by N-heterocyclic carbenes (NHC) towards reductive elimina-



Scheme 23. Proposed mechanism for the formation of methyl iodide from (IPr)AuI$_2$Me.

tion of C(sp^3)–X (X = I, F) bond has been recently investigated. Bercaw, Labinger, and Scott prepared the *trans*-(IPr)AuI$_2$Me complex (IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) by oxidation of (IPr)AuMe with I$_2$, and studied its decomposition to methyl iodide and (IPr)AuI by ^{1}H NMR spectroscopy (Scheme 23).[68] Kinetic studies revealed a dependence of the decomposition rate on the I$^-$ concentration; addition of a small amount of LiI was shown to slow down the formation of MeI. A dissociative pathway involving dissociation of iodide from *trans*-(IPr)AuI$_2$Me followed by reductive elimination from a transient three-coordinate intermediate was proposed to account for the Me–I bond formation.

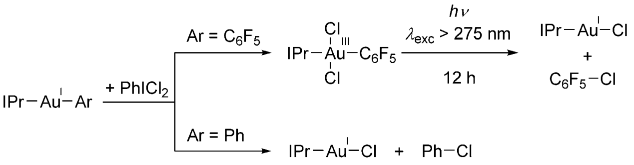
Toste and Mankad studied the kinetics of the C(sp^3)–F reductive elimination from *cis*-F$_2$(IPr)Au(alkyl) complexes and proposed a similar dissociative pathway.[69] Several gold(III) fluoride intermediates, generated by oxidation of (IPr)Au(alkyl) complexes with XeF$_2$, could be detected by ^{19}F NMR spectroscopy. Notably, alkylgold(III) fluoride complexes were shown to exhibit longer lifetimes than analogous iodide derivatives. While the *trans*-I$_2$(IPr)Au(Me) complex[68] undergoes rapid reductive elimination, the related *cis*-F$_2$-(IPr)Au(Me) complex is highly stable.[70] Depending on the nature of the alkyl group, the C(sp^3)–F bond reductive elimination was shown to be in competition with side-reactions, such as β-hydride elimination or carbocation rearrangement (Wagner–Meerwein; Scheme 24). The proposed three-coordinate intermediates [(IPr)Au(F)(R)]$^+$ could not be characterized directly but the *cis*-F$_2$(IPr)Au(Me) complex was shown to be in equilibrium with a F-bridged dimeric complex of [(IPr)Au(F)(Me)]$^+$, supporting the feasibility of fluoride dissociation from gold.[70]



Scheme 24. Proposed dissociative mechanism for C(sp^3)–F bond reductive elimination from (IPr)alkylgold(III) fluorides, and influence of the alkyl group on the selectivity of the process.

3.2.2. *C(sp^2)–X and C(sp^2)–N Bond Formation*

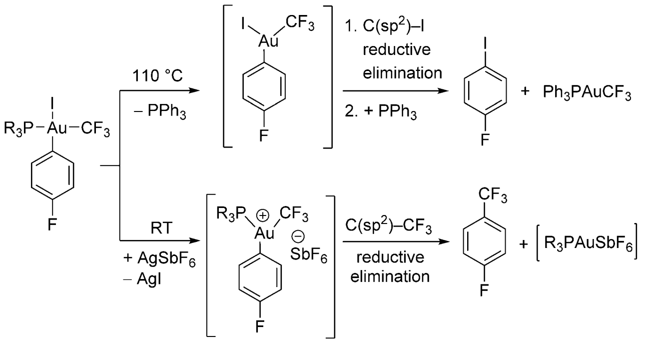
Reductive elimination of C(sp^2)–X (X = Cl, I) bonds from four-coordinate arylgold(III) complexes has also been investigated recently. Rosenthal and co-workers treated (IPr)arylgold(I) complexes (Ar = Ph or C$_6$F$_5$) with PhICl$_2$ (Scheme 25).[71,72] The *trans*-(IPr)AuCl$_2$(C$_6$F$_5$) complex obtained is stable at room temperature, but slowly decomposes upon exposure to light. The reductive elimination of C$_6$F$_5$–Cl was triggered by irradiating a solution of the gold(III) complex in CHCl$_3$. By analogy with C(sp^3)–X bond reductive eliminations, dissociation of chloride was proposed to occur before C(sp^2)–Cl bond reductive elimination. Reaction of (IPr)AuPh with PhICl$_2$ directly gives chlorobenzene, without detection of a gold(III) species.



Scheme 25. C(sp^2)–Cl bond formation upon reaction of (IPr)AuAr complexes with PhICl$_2$.

Toste and co-workers studied the stability of the four-coordinate aryl gold(III) complex Au(4-F-C$_6$H$_4$)(CF$_3$)I(PPh$_3$) (Scheme 26), which was prepared by oxidative addition of CF$_3$I to gold(I) (see Section 2). Reductive elimination proceeds at 110 °C in toluene over 20 minutes and leads selectively to C(sp^2)–I bond formation. When PPh$_3$ is replaced by the stronger σ-donor ligand PCy$_3$, the corresponding gold(III) complex is stable at this temperature over 12 h. Moreover, the addition of a small amount of free PPh$_3$ to the reaction medium leads to complete inhibition of the decomposition process. Interestingly, although the iodide and aryl groups are in *trans* position to each other,[64] the reductive elimination is fully selective towards C(sp^2)–I over C(sp^2)–CF$_3$ bond formation under these conditions.[73]

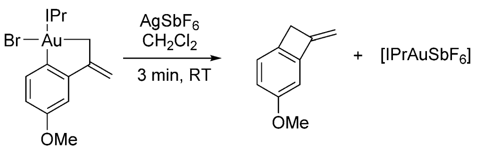
Overall, these observations also suggest a dissociative mechanism involving transient formation of a three-coordinate [Au(aryl)(CF$_3$)I] intermediate for which the C(sp^2)–I reductive elimination is much more favored (Scheme 26). The C(sp^2)–CF$_3$ reductive elimination is observed only upon iodide abstraction by a silver salt



Scheme 26. Reductive elimination of C(sp^2)–I and C(sp^2)–CF$_3$ bonds from Au(aryl)(CF$_3$)I(PR$_3$) complexes (R = Cy, Ph).

(Scheme 26, lower path). Monitoring the reaction by NMR spectroscopy indicated spontaneous C(sp^2)–CF$_3$ bond formation, even at -10°C with PCy$_3$ ligand, and no three-coordinate cationic gold(III) intermediate [Au(aryl)(CF$_3$)(PR$_3$)]$^+$ was detected.

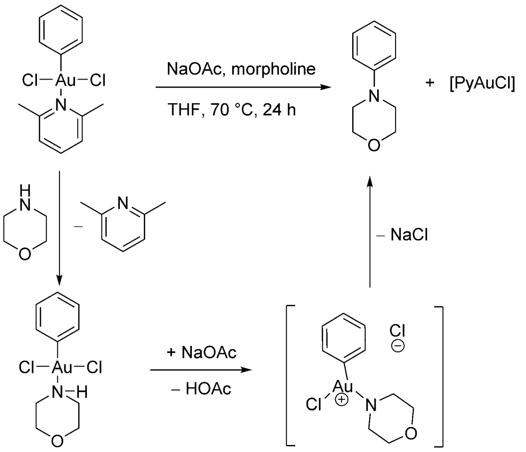
C(sp^2)–Br reductive elimination has also been studied starting from a cycloaurated gold(III) complex (Scheme 27).[22] Cyclometalation imparts high stability to the four-coordinate Au^{III} complex and no reductive elimination is observed upon heating. In contrast, abstraction of the bromide with AgSbF$_6$ afforded a putative cationic three-coordinate intermediate that spontaneously undergoes intramolecular C(sp^2)–C(sp^3) bond formation. Notably, the formation of the benzocyclobutane was shown to be quantitative despite the strain of the resulting four-membered ring.



Scheme 27. C(sp^2)–C(sp^3) reductive elimination upon bromide abstraction from a cyclometalated four-coordinate gold(III) complex.

Limbach and co-workers investigated C(sp^2)–N bond reductive elimination by reacting a four-coordinate dichloro(lutidine)phenylgold(III) complex with morpholine (Scheme 28).[74] Lutidine is first displaced by morpholine at gold. In the presence of NaOAc, the bound morpholine would then be deprotonated, followed by dissociation of a chloride ligand. The resulting cationic three-coordinate amido(phenyl)Au^{III} chloride intermediate (not detected) would undergo fast C(sp^2)–N reductive elimination. Of note, the competitive C(sp^2)–Cl bond formation was not observed, suggesting that C(sp^2)–N reductive elimination would be more favored under these conditions.

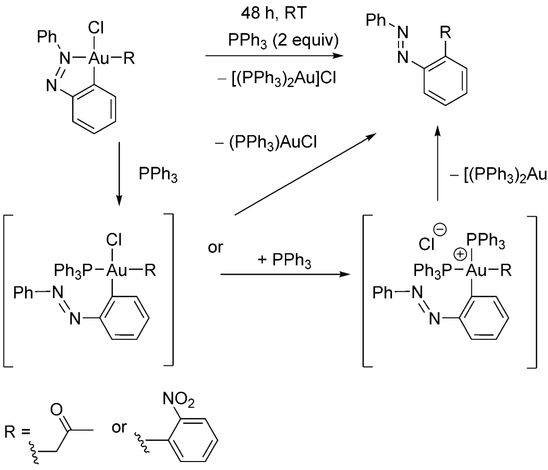
Thus, reductive eliminations of C(sp^2)–X, C(sp^3)–X, C(sp^3)–C(sp^3), and C(sp^2)–C(sp^3) bonds from four-coordinate organogold(III) complexes have been reported. The mechanistic studies indicate that the generation of a transient three-coordinate gold(III) species by ligand dissociation or halide abstraction is a prerequisite for the reductive elimination to take place. As discussed hereafter, a few examples of direct reductive elimination from four-coordinate gold(III) complexes have also been authenticated in the case of C(sp^2)–C(sp^2) bond of formation.



Scheme 28. Proposed mechanism for a C(sp^2)–N bond-forming reaction via reductive elimination from a gold(III) complex.

3.3. Reductive Elimination from Tetracoordinate Gold(III) Complexes

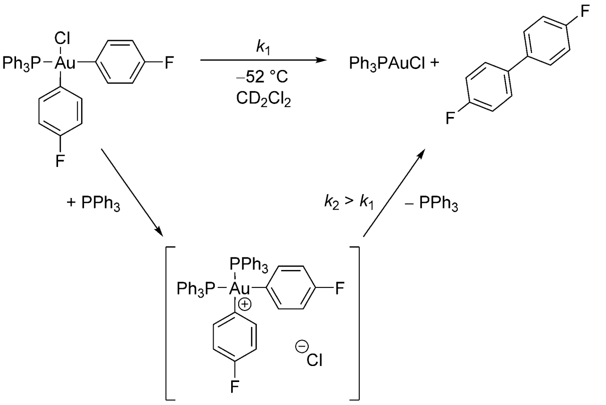
In the early 1990s, Vicente et al. reported bis(aryl)gold(III) or aryl[(α-keto)alkyl]gold(III) complexes featuring a chelating *o*-metallated phenylazo ligand (Scheme 29).[75]



Scheme 29. Proposed mechanism for aryl–aryl or aryl–alkylketone coupling from organogold(III) complexes with postulated intermediates.

These complexes undergo C–C bond reductive elimination in refluxing THF. The addition of two equivalents of PPh$_3$ allowed the C–C coupling to occur at room temperature.[76,77] The reactivity of these complexes is in stark contrast to that of alkylgold(III) species for which traces of added phosphine inhibit the reductive elimination. Excess of PPh$_3$ was proposed to displace the azo group and eventually a chloride ligand at gold, and the C–C bond reductive elimination was suggested to occur directly from four-coordinate gold(III) species.

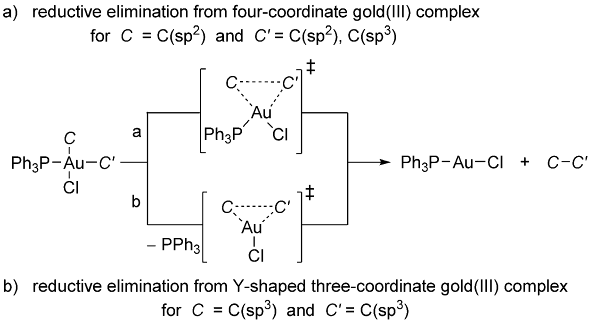
Toste and co-workers recently reported kinetic investigations on a very facile $C(sp^2)$–$C(sp^2)$ bond reductive elimination from *cis*-bis(aryl)gold(III) complexes.[78] The bis(aryl)gold(III) species was prepared in situ by oxidation of $Au(p\text{-}F\text{-}C_6H_4)(PPh_3)$ with phenyliodoso dichloride, followed by transmetallation employing a second equivalent of the arylgold(I) complex at −78 °C. The gold(III) species was identified by ^{31}P and ^{19}F NMR spectroscopy at low temperature. Remarkably, a very fast decomposition of the gold(III) species to $AuCl(PPh_3)$ and difluorobiphenyl was evidenced by NMR spectroscopy at −52 °C (Scheme 30). This reaction stands among the fastest transition-metal-mediated C–C coupling reactions!



Scheme 30. Facile biaryl reductive elimination from gold(III) phosphine complexes.

Interestingly, the reaction rate is significantly increased upon addition of an excess of phosphine. In contrast, addition of NBu_4Cl has no influence. These observations indicate that the mechanism for the reductive elimination of $C(sp^2)$–$C(sp^2)$ bonds differs from that observed for $C(sp^3)$–$C(sp^3)$ bonds. The biaryl formation occurs readily from a four-coordinate gold(III) species, and does not require phosphine dissociation. The excess of PPh_3 is proposed to rapidly displace the chloride ligand to generate a transient cationic $(Ph_3P)_2$bis(aryl)gold(III) species that decomposes much faster (Scheme 30).Aryl–aryl bond formation from bimetallic Au^{II} complexes was also investigated, and showed that these species can undergo very fast isomerization to Au^{I}/Au^{III} species followed by reductive elimination from the gold(III) center at low temperature.

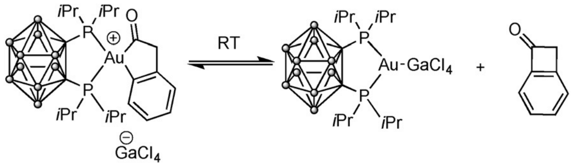
Subsequently, the mechanism of C–C bond reductive elimination from four-coordinate gold(III) phosphine complexes was examined computationally by Datta and co-workers.[79] DFT calculations indicated kinetically facile reductive elimination via a concerted mechanism in all cases, except for $C(sp^3)$–$C(sp^3)$ bond formation. Faster reductive elimination was predicted for the cationic $[Au(PPh_3)_2(4\text{-}F\text{-}C_6H_4)_2]^+$ species than for the neutral $AuCl(4\text{-}F\text{-}C_6H_4)_2(PPh_3)$ complex, in line with experimental observations. The energy barrier computed for C–C bond coupling was shown to gradually increase depending on carbon hybridization, from $\Delta H^{\neq} = 16.1$ kcal mol^{-1} for $C(sp^2)$–$C(sp^2)$, to 24.9 kcal mol^{-1} for $C(sp^3)$–$C(sp^2)$, and 35.7 kcal mol^{-1} for $C(sp^3)$–$C(sp^3)$. In the $C(sp^3)$–$C(sp^3)$ case, the most favorable pathway involves phosphine decoordination to give a Y-shaped tricoordinate gold(III) intermediate ($\Delta H^{\neq} = 16.0$ kcal mol^{-1}, Scheme 31), in line with the early mechanistic proposals of Kochi, Tobias, and Komiya.



Scheme 31. Distinct mechanisms for $C(sp^3)$–$C(sp^3)$ reductive elimination (lower path) and for $C(sp^3)$–$C(sp^2)$ or $C(sp^2)$–$C(sp^2)$ reductive elimination (upper path).

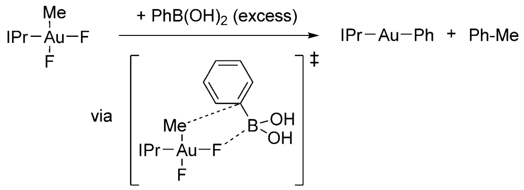
The electronic properties of aryl groups significantly influence the barriers of $C(sp^2)$–$C(sp^2)$ reductive eliminations. Faster rates were predicted with electron-rich arenes and consistently, C_6F_5–C_6F_5 reductive elimination from the isolated $AuCl(C_6F_5)_2(PPh_3)$ complex was a slow process even at high temperature (150 °C, 20 h).[80]

Finally, Amgoune, Bourissou, and co-workers recently reported that the activation of the $C(sp^2)$–C(O) bond of benzocyclobutenone at $[(DPCb)Au]^+$ complexes is a reversible process, providing direct evidence for $C(sp^2)$–C(O) bond reductive elimination from a cationic four-coordinate gold(III) complex.[54] Upon dissolving in dichloromethane, the isolated cyclometallated gold(III) complex supported by a diphospino carborane ligand evolves spontaneously back to the starting materials (Scheme 32).



Scheme 32. Spontaneous reductive elimination of a $C(sp^2)$–C(O) bond from a well-defined four-coordinate cationic gold(III) complex.

Noteworthy, an alternative pathway for C–C bond formation from gold(III) fluorides was proposed by Toste and Mankad.[70] In this case, the electronic properties of arylboronic acids have little effect on the rate of their reaction with methylgold(III) fluorides, leading to C(sp^3)–C(sp^2) bond formation. The coupling product was proposed to result not from intramolecular C–C bond reductive elimination, but rather from a concerted bimolecular outer-sphere mechanism, for which the C–C bond formation is assisted by coordination of one fluoride to boron (Scheme 33).



Scheme 33. Proposed bimolecular reductive elimination of toluene from a gold(III) fluoride and phenylboronic acid via a concerted outer-sphere mechanism.

Overall, these studies show that reductive elimination from tetracoordinate gold(III) complexes proceeds via two mechanistic pathways, depending on the nature of the bond to be formed. The reductive elimination of C(sp^2)–X, C(sp^3)–X (X = halogen), C(sp^2)–C(sp^3), and C(sp^3)–C(sp^3) bonds occurs from three-coordinate gold(III) intermediates after ligand dissociation, while reductive elimination of C(sp^2)–C(sp^2) bonds proceeds directly from four-coordinate (bis)arylgold(III) complexes.

Although these contributions have provided important insight into the mechanism of C–X and C–C bond reductive eliminations at gold, additional studies are clearly needed to gain a more comprehensive mechanistic picture, to delineate the scope of the reaction and to precisely determine the influence of electronic/steric parameters. For instance, the proposed three-coordinate gold(III) intermediates have not been directly observed to date. The selectivity of reductive elimination reactions also raises several questions. In this perspective, one of the main shortcomings to overcome is the limited synthetic access to a broad range of appropriate gold(III) complexes. Indeed, many of the reported studies have been carried out with unstable gold(III) species generated in situ by oxidation of dicoordinate gold(I) complexes. The access to well-defined gold(III) complexes via C–X and C–C oxidative additions, as described in Section 2, will certainly give more insight into the key factors influencing the rate and selectivity of reductive elimination processes.

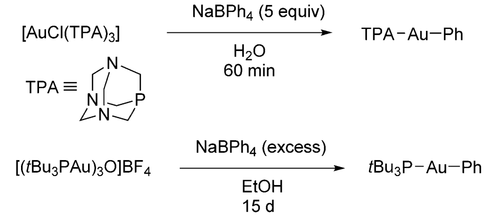
4. Transmetallation/Metallation (C–H Activation) Reactions

Transmetallation plays a central role in a wide range of coupling reactions. It is the key step in which an organic fragment is transferred from a coupling reagent (an organometallic nucleophilic derivative or even a simple arene) to a transition-metal species. Transmetallation reactions have been documented between gold and a variety of transition metals under stoichiometric and catalytic conditions.[15,81–88] Most noticeable is the development of bimetallic catalysis involving organogold species as co-catalysts, which act as transmetallating agents and transfer organic fragments to other transition metals, typically Pd.[89] This reactivity of organogold complexes has been recently reviewed,[86] and thus is not discussed herein. This Section actually focuses on transmetallation reactions of p-block elements (boron, silicon, and tin reagents) to gold complexes, and on direct C–H auration reactions.

4.1. Transmetallation between Gold Complexes and Boron Derivatives

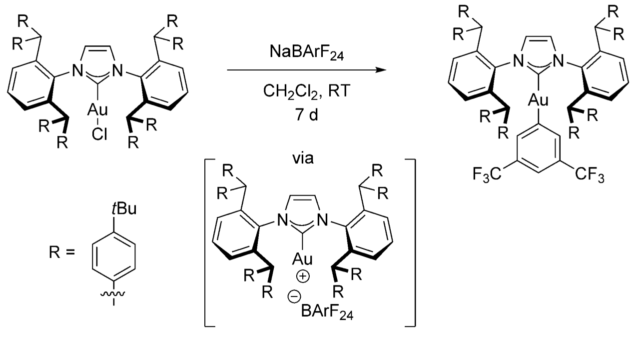
4.1.1. Reaction with Borate Species

Early evidence for transmetallation of an aryl group from boron to gold was independently reported by the Schmidbaur and Fackler groups (Scheme 34).[90,91] Sodium tetraphenylborate was shown to readily transfer a phenyl group to gold(I) and the (TPA)AuPh complex was obtained accordingly (TPA = 1,3,5-triaza-7-phosphaadamantane). A similar, albeit slower reaction was observed starting from a trinuclear gold oxide.



Scheme 34. Seminal reports on boron-to-gold transmetallation with sodium tetraphenylborate.

A related boron-to-gold aryl transfer was reported more recently by Straub and co-workers upon reaction of a sterically hindered NHC-gold(I) chloride complex with NaBArF$_{24}$ (BArF$_{24}^-$ = tetrakis[bis(3,5-trifluoromethyl)phenyl]borate).[92] NMR monitoring suggested the transient formation of a cationic NHC-gold(I) complex, which would slowly abstract an aryl group from the weakly coordinating borate anion (BArF$_{24}^-$) at room temperature (Scheme 35). This

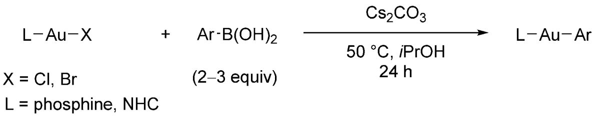


Scheme 35. Transmetallation of a bis(trifluoromethyl)phenyl group from boron to gold(I).

reactivity underlines the extreme electrophilic character of cationic monoligated gold(I) complexes.

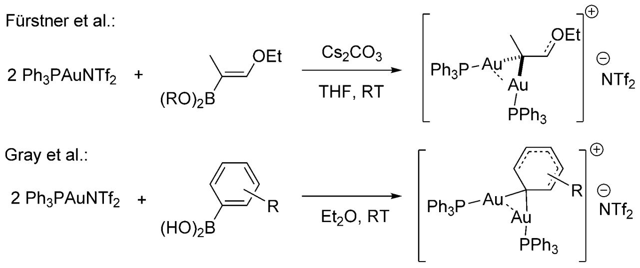
4.1.2. Reaction with Boronic Acids

Transmetallation from arylboronic acids to gold has been demonstrated with a series of Au^{I} and Au^{III} complexes. Gray and co-workers developed an efficient method for the synthesis of arylgold(I) compounds by treating arylboronic acids with LAuX complexes (L = phosphine or NHC, X = Cl or Br) in the presence of a mild base (Scheme 36).[93,94] Quantitative yields are obtained upon heating the reaction mixture at 50 °C for 24 h. Further optimization of the reaction conditions employing microwave irradiation led to shorter reaction times.[95] A large variety of aryl and vinyl groups can be efficiently transferred to gold(I), including aryl groups that are not compatible with Grignard or lithium reagents.[94,96–100]



Scheme 36. Synthesis of arylgold(I) complexes via B-to-Au transmetallation.

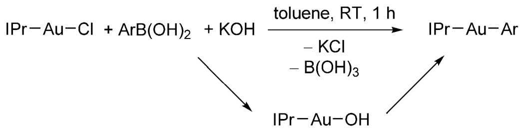
Interestingly, the reaction of two equivalents of phosphine gold(I) triflimidate complex with either vinyl or aryl boronic ester in the presence of Cs$_2$CO$_3$ affords the corresponding *gem*-digold vinyl[101] and *gem*-digold aryl species,[102] respectively (Scheme 37).



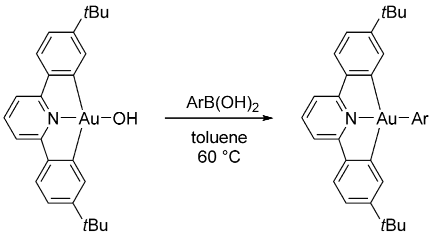
Scheme 37. Synthesis of *gem*-digold vinyl and *gem*-digold aryl complexes via B-to-Au transmetallation.

The Nolan group studied the reaction of arylboronic acids with AuCl(IPr) in more detail.[103] The use of potassium hydroxide instead of Cs$_2$CO$_3$ enables the transmetallation to be performed at room temperature. The reaction was proposed to involve the formation of gold(I) hydroxide species as the key intermediate (Scheme 38), although an alternative route with participation of a borate was not excluded.

The reactivity of gold hydroxide species in B-to-Au transmetallation was confirmed by Bochmann and co-workers by treating an isolated (CNC)pincer gold(III)-OH complex with boronic acids.[104,105] The hydroxide complex reacts directly with both electron-rich and electron-poor aryl boronic acids in toluene at 60 °C to give the corresponding (CNC)gold(III) aryl species (Scheme 39).

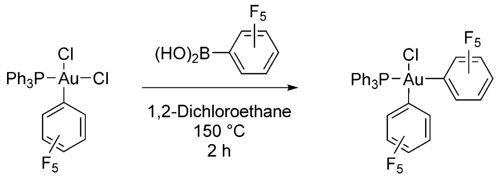


Scheme 38. B-to-Au transmetallation promoted by KOH.



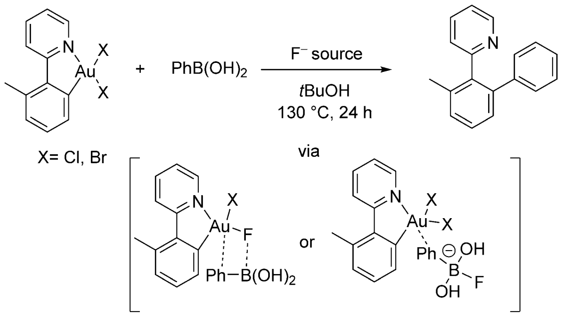
Scheme 39. Aryl transfer from boronic acids to (CNC)gold(III) hydroxide complex. Ar = *p*-F-C$_6$H$_4$, *p*-*t*Bu-C$_6$H$_4$, furyl; acenaphthenyl, thiophenyl, benzothiophenyl.

As shown by Nevado and co-workers, B-to-Au aryl transfer can also proceed in the absence of base in the case of gold(III) dichloride complexes. However, the reaction requires forcing conditions (150 °C) and works only with electron-poor arylboronic acids (Scheme 40).[80] On the basis of DFT studies, a stepwise mechanism involving chloride abstraction from gold followed by migration of the aryl group from boron to gold(III) was proposed.[106]



Scheme 40. Transmetallation of electron-deficient aryl between boronic acids and a gold(III) chloride complex.

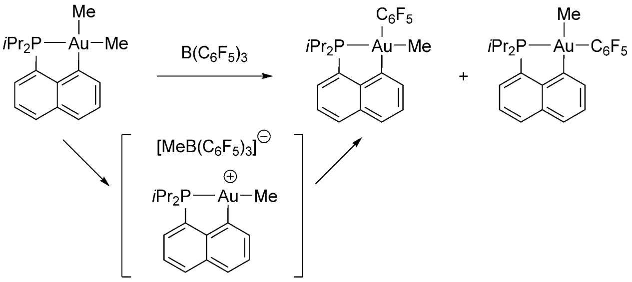
The You group reported mechanistic studies on the reaction of C,N-cyclometallated Au^{III}X$_2$ (X = Br, Cl) complexes with arylboronic acids in the presence of fluoride sources.[107] The reaction proceeds in stoichiometric and catalytic conditions (with external oxidant) and results in C−C coupling of the aryl fragment of ArB(OH)$_2$ and the C,N ligand (Scheme 41). The fluoride source was proposed to assist B-to-Au transmetallation via the formation of Au^{III} fluoride or fluoroborate species.[108]



Scheme 41. Reaction of (C,N)Au^{III}X$_2$ complexes with PhB(OH)$_2$ in the presence of fluoride.

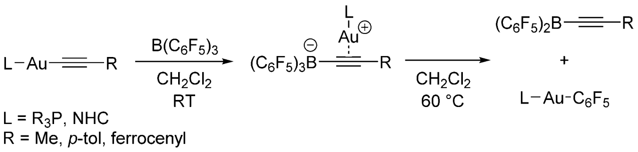
4.1.3. Reaction with boranes

The reactivity of organogold species with the strong Lewis acid tris(pentafluorophenyl)borane B(C$_6$F$_5$)$_3$ has been explored recently to generate cationic gold species (as an alternative strategy to halide abstraction with silver salts). Amgoune, Bourissou, and co-workers studied the reaction of a cyclometallated (P,C)Au^{III}Me$_2$ complex with B(C$_6$F$_5$)$_3$ with the aim of abstracting a methide and generate a cationic gold(III) methyl complex.[109] Instead, clean formation of two (P,C)Au^{III}Me(C$_6$F$_5$) isomers was observed. By analogy with the observations of Straub, the Me/C$_6$F$_5$ redistribution probably proceeds via methide abstraction to form a transient tricoordinate cationic gold(III) methyl complex, and subsequent abstraction of a C$_6$F$_5$ group from the boron center (Scheme 42).



Scheme 42. Me/C$_6$F$_5$ redistribution upon reaction of a P,C-cyclometallated Au^{III}Me$_2$ complex with B(C$_6$F$_5$)$_3$.

A related alkyne/C$_6$F$_5$ exchange between (L)gold(I) acetylides (L = NHC or phosphine) and B(C$_6$F$_5$)$_3$ has been reported by Hansmann, Stephan, and Hashmi.[110] The reaction proceeds via abstraction of the alkynyl fragment by B(C$_6$F$_5$)$_3$ to form the corresponding alkynyl borate species, in which the alkyne is π-coordinated to the [(L)Au]$^+$ fragment (Scheme 43). This σ-B/π-Au species was isolated and fully characterized. After prolonged heating at 60 °C, one C$_6$F$_5$ group is transferred to the cationic gold fragment to give the (NHC)Au-C$_6$F$_5$ complex. The same type of alkyne/aryl exchange process was found using PhB(C$_6$F$_5$)$_2$ or BPh$_3$, though the σ-B/π-Au intermediate could not be detected in these cases. The reaction between (NHC)gold aryl species



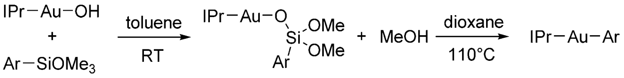
Scheme 43. Alkyne/C$_6$F$_5$ exchange between gold acetylides and B(C$_6$F$_5$)$_3$

and B(C$_6$F$_5$)$_3$ follows a different route and results in cationic *gem*-diaurated gold(I) species [(LAu)$_2$Ar]$^+$,[ArB(C$_6$F$_5$)$_3$]$^-$.

4.2. Transmetallation between Gold Complexes and Group 14 Compounds

4.2.1. Reaction with Silanes

Nolan and co-workers recently reported a fluoride-free transmetallation of organosilanes to gold.[111] (IPr)gold hydroxide complexes react with aryltrimethoxysilanes at room temperature to give (IPr)arylgold complexes (Scheme 44).

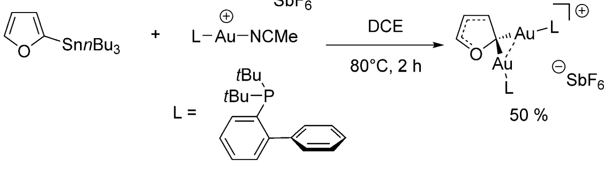


Scheme 44. Synthesis of arylgold complexes by Si-to-Au transmetallation, starting from gold hydroxides and involving gold silanolate complexes.

The reaction proceeds through gold silanolate intermediates that can be isolated and characterized. The Si-to-Au transmetallation proceeds best in 1,4-dioxane and presumably involves pentacoordinate Si species. The process shows good functional group tolerance and works also for vinyl and allyl transfer.

4.2.2. Reaction with Stannanes

As part of mechanistic investigations on gold-catalyzed cycloisomerization/stannylation of 1,6 diyne-4-enols, Liu performed Sn-to-Au transmetallation and isolated thereby a *gem*-diaurated furyl complex (Scheme 45).[112] Transmetallation of organic fragments between tin reagents and gold intermediates has been explored in the context of Au/Pd catalysis. Transmetallation of organic fragments from tin to



Scheme 45. Transmetallation from an organostannane to a cationic gold complex.

gold has also been explored in the context of Au/Pd catalysis. Blum's group first reported that $(Ph_3P)AuSbF_6$ can act as a transmetallation shuttle between tin and palladium in the carbostannylation of alkynes.[82,83] Then, Casares, Espinet, and co-workers showed the ability of $(Ph_3E)AuX$ (E = P, As; X = Cl, I) to promote Sn-to-Pd transmetallation and Au/Pd systems proved to be particularly efficient at catalyzing the Stille coupling of bulky substrates.[89]

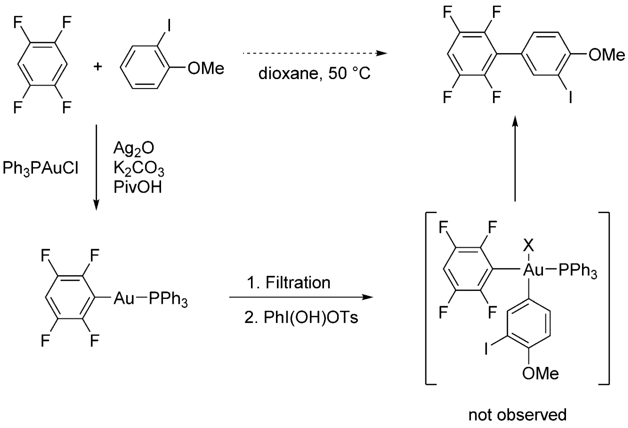
Overall, these examples show that organogold(I) and gold(III) complexes can be readily accessed by transmetallation of organic fragments from boron, silicon, or tin derivatives. Different mechanistic pathways have been proposed depending on the nature of the transfer agent and the operating conditions. Up to date, the scope of organic fragments transferred from *p*-block elements to gold is mostly limited to aryl moieties, and occasionally to vinyl ones. Access to alkyl gold species by transmetallation has still to be developed.

4.3. Direct C–H Auration

Another strategy to access aryl gold complexes is the direct C–H activation of simple arenes. Gold(III) salts were recognized early on to readily perform C(sp^2)–H bond activation.[113] These aurations are more appealing than classical transmetallation reactions, which require pre-functionalization of the C–H bond into a more reactive organometallic derivative. Catalytic C–H bond functionalization processes have been developed with gold and several Reviews summarize the recent achievements in this field.[11d,114–116] The following discussion is focused on selected recent reports that have provided fundamental insight into C–H bond activation at gold.

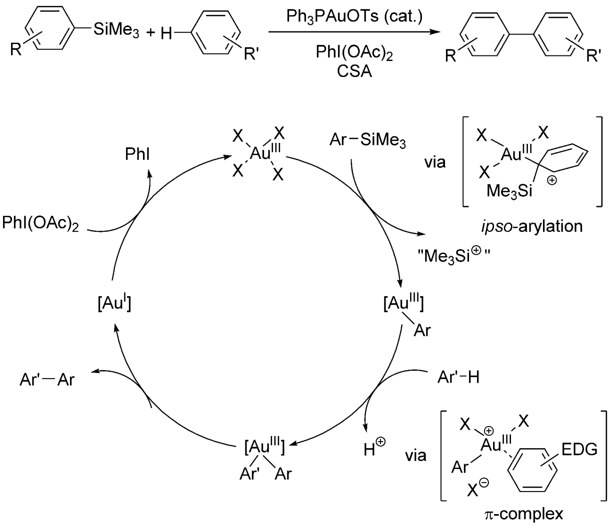
Different mechanistic pathways have been proposed, depending on the oxidation state of gold. With gold(III) complexes, C–H bond activation is generally proposed to occur via electrophilic activation (S_EAr-type pathway) and only electron-rich arenes readily react.[11d,117] In contrast, gold(I) complexes preferentially activate electron-deficient arenes and the auration proceeds in this case via concerted metalation–deprotonation (typical conditions involve a silver salt, a mild base, and pivalic acid).[118]

Based on the orthogonal reactivity of Au^I/Au^{III} complexes towards C–H activation,[11d,119,120] Larrosa's group developed a stoichiometric oxidative cross-coupling reaction of electron-poor and electron-rich arenes (Scheme 46).[119] Selective auration of the electron-poor arene is first achieved with a phosphine gold(I) complex in the presence of Ag_2O and K_2CO_3. After separation from the silver and potassium salts, the resulting arylgold(I) was treated with hydroxy(phenyl)iodonium tosylate to give selectively the cross-coupling product. It was proposed that the in situ generated aryl gold(III) species undergoes selective C–H activation of the electron-rich arene to give a bis(aryl)gold(III) complex and subsequent reductive elimination.



Scheme 46. Sequential Au^I–Au^{III} C–H bond activation, followed by reductive elimination yielding biaryls.

The discovery by Lloyd-Jones, Russell, and Ball of gold-catalyzed coupling reactions between simple arenes and aryltrimethylsilanes represented a major breakthrough.[120] The reaction was meticulously studied by means of kinetic analyses,[121] and a simplified representation of the catalytic cycle is depicted in Scheme 47. The active species is a "ligand-free" gold(III) derivative generated in situ by oxidation. The reaction would occur via consecutive electrophilic arylation (S_EAr) of the arylsilane and of the arene, and subsequent reductive elimination. High selectivity for heterocoupling versus homocoupling is found, particularly with electron-rich arenes. It was proposed that the first auration occurs selectively on the arylsilane (the silyl group is activating and it orientates the reaction to the *ipso* position) while the second auration is controlled by π-coordination of the electron-rich arene.



Scheme 47. Simplified catalytic cycle for the gold-catalyzed direct arylation of arylsilanes with proposed key intermediates.

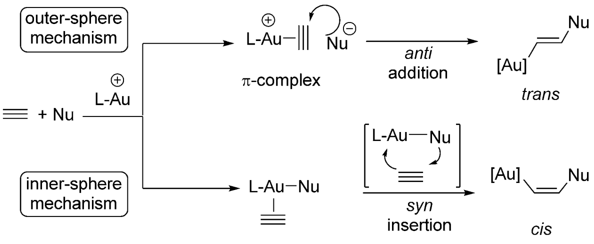
The ability of gold complexes, particularly gold(III) species, to perform C(sp^2)–H bond auration has been shown, but it is still limited to a few examples. To date, only sparse information has been gained on the mechanism (S_EAr

vs. CMD) of C–H auration and on the key factors controlling it. Well-defined gold(III) complexes will certainly contribute to developing this field and to gaining better understanding of the parameters governing the efficiency and selectivity of C–H auration. Further studies are also required to delineate conditions in which the transformations can be extrapolated from stoichiometric to catalytic versions.

5. Migratory Insertion and Miscellaneous Reactions

Migratory insertion is a fundamental reaction in organometallic chemistry, known for all the transition metals. This elementary step is at the basis of many important catalytic processes involving the functionalization, derivatization, or coupling of unsaturated substrates (such as, olefins, alkynes, ketones, imines).

Over the last few years, migratory insertion of C–C multiple bonds at gold has been frequently considered as a possible pathway to account for gold-catalyzed functionalization reactions.[6,122–124] In particular, thorough mechanistic studies have been carried out on the gold-catalyzed hydroamination of alkynes,[125–129] allenes,[127,130–132] and alkenes.[133,134] Although some reports suggested an inner-sphere insertion pathway (i.e. migratory insertion of the π-substrate into a Au–N bond to give a *cis* vinyl gold complex, Scheme 48),[125,126,128,130] most experimental and computational data support an outer-sphere mechanism (nucleophilic attack of the π-complex *anti* to gold, affording a *trans* vinyl gold complex, Scheme 48).[6,135] Furthermore, isolated NHC-gold(I) amide[136] and phenoxide[137] complexes have been shown not to react with alkynes even at high temperatures. Thus these compounds are unlikely intermediates in gold-catalyzed addition of O and N nucleophiles to π-substrates.

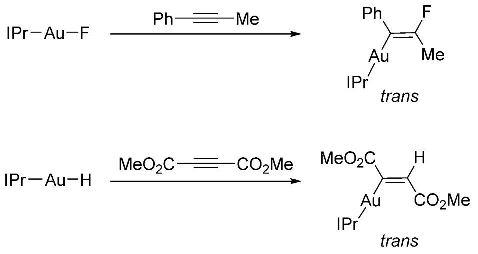


Scheme 48. Schematic representation of the outer- and inner-sphere mechanisms for the gold catalyzed addition of nucleophiles to alkynes.

In parallel, fundamental studies have been carried out recently on the reaction of well-defined gold(I) and gold(III) complexes with alkynes, alkenes, and allenes. Accordingly, stoichiometric insertion reactions into a variety of Au–X bonds (X = H, C, O, F, Si) have been found.

5.1. Stoichiometric Insertion Reactions with Gold(I) Complexes

Sadighi and co-workers reported the insertion of alkynes into Au–F and Au–H bonds of NHC-gold(I) fluoride[138] and hydride[139] complexes. The resulting vinylgold complexes display *trans* arrangement (Scheme 49), excluding a one-step *syn* insertion mechanism. For the gold(I) fluoride, the reaction is likely to proceed via displacement of the fluoride, and subsequent nucleophilic *anti* addition to the π-coordinated alkyne. Insertion of the electron-deficient alkyne into the Au–H bond was proposed to occur either by a radical mechanism or by a *syn* insertion/isomerization process.

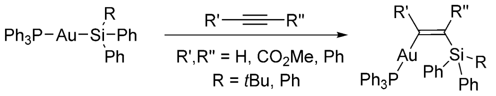


Scheme 49. Stoichiometric reactions between alkynes and NHC-gold fluoride and NHC-gold hydride complexes.

The NHC-gold(I) hydride does not react with terminal and non-activated alkynes. Hashmi, Köppel, and co-workers also reported that olefins, such as ethylene or norbornene, do not insert into the Au–H bond even upon heating. In fact, computational studies indicated that the insertion of olefins into gold(I)-hydrogen bonds involves a huge activation barrier and requires prohibitively high temperatures ($>150\,^{\circ}C$).[140]

Thus, two-coordinate gold(I) complexes, if reactive towards unsaturated substrates, do not react via an inner-sphere coordination–insertion mechanism.[141] As mentioned earlier (Section 2), the coordination of a third ligand to two-coordinate gold(I) complexes is strongly disfavored,[40–57] owing to a high deformation energy.[40,53] This represents a major hurdle for the establishment of migratory insertion processes with gold(I) complexes.

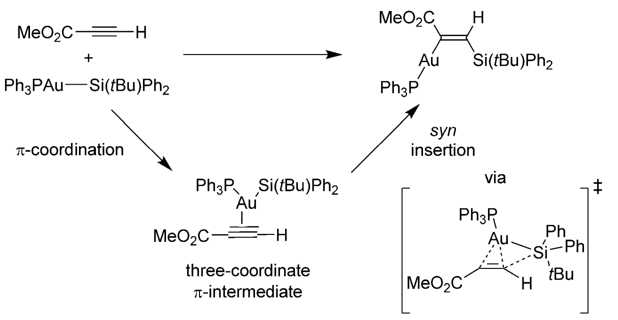
A noticeable exception pertains to gold(I) silyl complexes. Amgoune, Bourissou, and co-workers recently reported that internal and terminal alkynes, as well as allenes readily insert in a *syn* fashion into the Au–Si bonds of $(Ph_3P)Au(SiPh_2R)$ complexes (Scheme 50).[142]



Scheme 50. Selective *syn* insertion of alkynes into the Au–Si bond of phosphine gold(I) silyl complexes

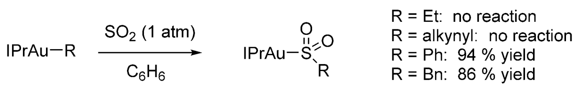
The resulting β-silyl vinylgold complexes were isolated and structurally characterized, revealing a *cis* arrangement of the gold and silicon atoms in all cases. The mechanism of the reaction was thoroughly investigated by a joint experimental/computational approach.[142b] Kinetic experiments indicated that the reaction is first-order in alkyne and gold silyl complex. Miqueu explored several mechanistic approaches by DFT calculations, including direct 1,2-addition of the Au–

Si bond to the alkyne with or without phosphine dissociation. The most favorable pathway was found to involve a two-step coordination–insertion process. The alkyne first coordinates to the phosphine gold(I) silyl complex to form a tricoordinate π-complex, followed by migratory insertion (rate-determining step; Scheme 51). The electronic properties of the silyl ligand, in particular its strong σ-donor character, play an important role in the formation of the π-complex intermediate and in the subsequent *syn* insertion.



Scheme 51. Two-step inner-sphere mechanism for the insertion of methyl propiolate into the Au–Si bond of phosphine gold(I) silyl complexes.

These results clearly indicate that the insertion of alkynes into gold–silyl bonds can proceed via an inner-sphere mechanism, and give credence to the mechanisms proposed to account for the functionalization of alkynes with (di)silanes catalyzed by gold nanoparticles.[143–145] Notably, the corresponding gold(I) methyl complex is inert towards alkynes. Organogold(I) complexes do not react with vinyl ketones,[99] and the only example of insertion into Au–C bonds refers to the reaction of sulfur dioxide (Scheme 52).[146] No reaction was observed with phenylacetylide and ethyl NHC gold complexes, but SO_2 readily inserted into Au–Ph and Au–CH_2Ph bonds at room temperature. The resulting gold sulfinate complexes were isolated in good yields and fully characterized. This elementary step was integrated in a multistep sequence involving B-to-Au transmetallation and ligand exchange, enabling the sulfination of arylboronic acids to be performed catalytically.

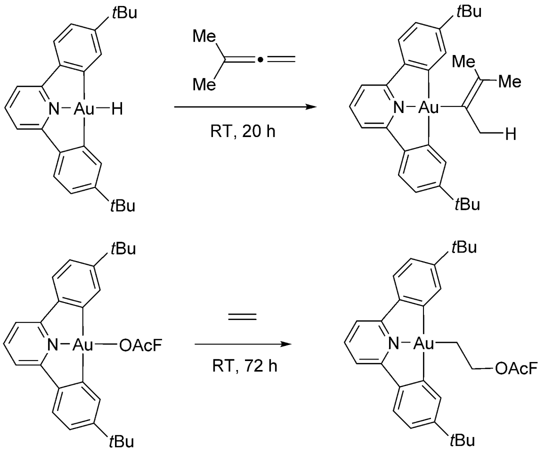


Scheme 52. Reaction of SO_2 with NHC-gold(I) carbon bonds.

5.2. Stoichiometric Insertion Reactions with Gold(III) Complexes

Owing to their unsaturated character (d^8 configuration), gold(III) complexes are promising candidates for migratory insertion. Although the low stability of gold(III) species has limited their exploration, the use of strongly chelating ligands has allowed significant progress over the last few years.[147] The coordination of alkenes to well-defined gold(III) complexes has been demonstrated, and detailed insights into the bonding situation have been gained.[148,149] A few recent reports have also substantiated the insertion of alkenes into Au^{III}–H, Au^{III}–O, and Au^{III}–C bonds.

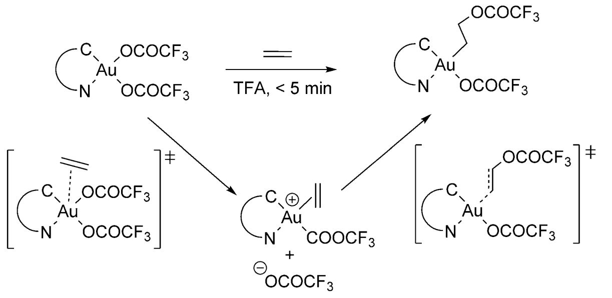
Bochmann and co-workers recently reported the synthesis and characterization of the first gold(III) hydride complex using a rigid C,N,C-pincer ligand based on 2,6-bis(4′-*tert*-butylphenyl)pyridine.[150,151] The hydride complex undergoes insertion reactions of allenes, yielding regioselectively Au^{III} vinyl complexes (Scheme 53). But in contrast to the NHC-gold(I) hydride complex reported by Sadighi, no reaction was observed with alkynes, or with ethylene. When the hydride is substituted by a trifluoroacetate ligand, slow but quantitative ethylene insertion into the Au^{III}–OAc^{F} ($\text{OAc}^{\text{F}} = \text{OCOCF}_3$) bond was observed at room temperature (Scheme 53).



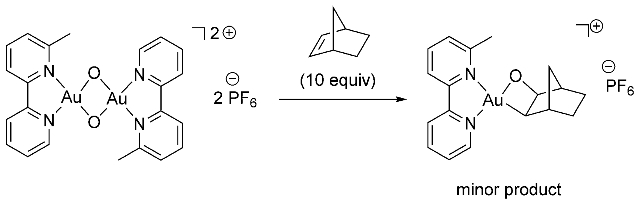
Scheme 53. Reactivity of a gold(III) hydride with allene (top) and gold(III) trifluoroacetate with ethylene (bottom).

The insertion of ethylene into the Au–OAc^{F} bond of a gold(III) complex with a C,N-cyclometalated 2-(*p*-tolyl)-pyridine ligand was thoroughly investigated by Tilset and coworkers.[152] According to X-ray diffraction analysis, ethylene inserts into the Au–O bond *trans* to the nitrogen atom of the C,N ligand. Experimental and theoretical investigations revealed that the reaction proceeds in two steps (Scheme 54). The OAc^{F} ligand *trans* to N is first displaced by ethylene via an associative mechanism to give the corresponding π-ethylene gold(III) complex. According to deuterium-labelling experiments, the second step occurs via *anti* addition of the free OAc^{F} anion to the coordinated olefin (outer-sphere). *Syn* insertion of the coordinated ethylene into the Au^{III}–OAc^{F} bond (inner-sphere) was found to be much less favorable.

During the study of dimeric gold oxo species, Cinellu et al. isolated and structurally characterized an original auraoxetane as a minor product of the reaction with norbornene (*syn* oxyauration, formal insertion of norbornene into Au^{III}–O bond; Scheme 55).[153]

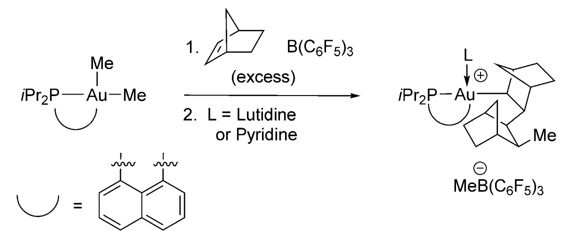


Scheme 54. Insertion of ethylene into the Au–OAc^F bond of a C,N-cyclometallated Au^{III}(OAc^F)$_2$ complex.



Scheme 55. Reaction of a gold-oxo species with norbornene.

Aiming at substantiating migratory insertion of olefins into gold–carbon bonds, Amgoune, Bourissou, and co-workers recently investigated the reactivity of P,C-cyclometallated gold(III) dimethyl complexes towards alkenes in the presence of $B(C_6F_5)_3$.[109] Depending on the nature of the olefin, a competitive Me/C_6F_5 transfer reaction occurred (see Section 4). While ethylene and styrene did not react under these conditions, norbornene (NB) readily inserted into the Au^{III}–C bond at low temperature. The resulting unstable cationic gold(III) norbornyl complex could be trapped with pyridines or chloride to give thermally stable four-coordinate gold(III) alkyl complexes (Scheme 56). X-ray diffraction analysis confirmed the insertion of two NB units from the *exo* face and in a *syn* manner, consistent with inner-sphere migratory insertion. These results demonstrate the ability of gold(III) alkyl complexes to undergo migratory insertion of olefins. Additional studies are needed to gain further mechanistic insight and generalize the process to other olefins.



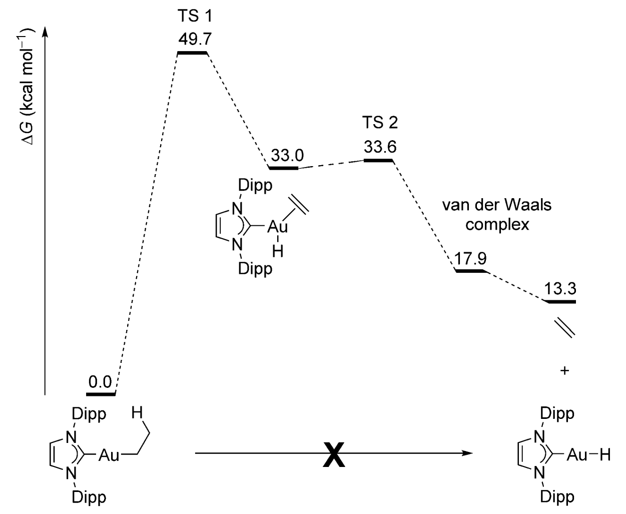
Scheme 56. Insertion of norbonene into Au^{III}–C bonds.

These recent results show that gold(III) complexes hold promise to establish new gold-mediated insertion processes, and the generation of relatively stable gold(III) complexes featuring both a migrating group and a free coordination site will certainly play a key role in future developments.

5.3. β-Hydride Elimination

β-hydride elimination occurs at metal alkyl complexes and is the microscopic reverse of olefin insertion into M–H bonds. The elimination of a hydrogen atom in β position of the metal generates a metal hydride species and an olefin. It is a transformation of high relevance in catalysis, often encountered as a side reaction in transformations involving metal alkyl complexes. While the propensity of late transition metals to undergo β-hydride elimination reaction is well established the reactivity of gold alkyl complexes is still poorly understood and gold complexes are usually considered as highly reluctant to undergo β-hydride elimination.[154] A very rare example is that observed by Toste and Mankad upon studying NHC alkylgold(III) fluoride complexes (see Section 3.2). In this case, the formation of alkenes as side-products suggested that β-hydride elimination competes with C–F reductive elimination.[69]

Köppel, Hashmi, and co-workers have studied β-H elimination at gold.[140] DFT calculations predicted a high barrier (49.7 kcal mol^{-1}) for the β-hydride elimination of ethylene from the (IPr)Au(Et) complex, with the formation of a high-energy three-coordinate ethylene gold(I) hydride species. Consistently, the (IPr)Au(Et) complex was shown experimentally to decompose only at around 180 °C, and probably not via β-hydride elimination (Scheme 57).



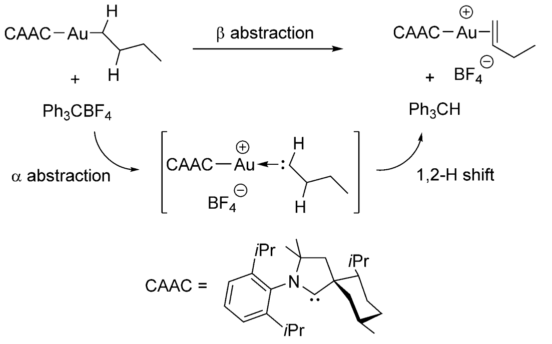
Scheme 57. Reaction profile computed for β-hydride elimination from an NHC-gold(I) ethyl complex. Dipp = (2,6-diisopropyl)phenyl.

The lack of reactivity of gold(I) complexes was attributed to the filled 5d shell, preventing the necessary C–H···Au interaction required for the elimination to take place.

According to a detailed analysis by Schmidbaur, Raubenheimer, and Dobrzańska of reported gold-hydrogen interactions, "*there is currently no evidence for agostic interactions in organogold compounds* […]".[155] Nevertheless, as suggested by Köppel and Hashmi, these interactions may exist in gold(III) alkyl complexes compounds,[140] and investigations in this direction are certainly worthwhile.

5.4. α- and β-Hydride Abstraction

In contrast to β-hydride elimination, α- and β-hydride abstractions have been shown by Bertrand to be a facile processes with gold(I) alkyl complexes.[156] Treatment of a (CAAC)gold(I) *n*-butyl complex with triphenylcarbenium tetrafluoroborate rapidly and quantitatively gives the corresponding 2-butene gold(I) complex. To differentiate between direct β-hydride abstraction and a two-step sequence involving α-hydride abstraction followed by 1,2-hydrogen shift, different alkyl groups (*tert*-butyl, neopentyl) were introduced at gold. Accordingly, hydrogen atoms in the β-position are more reactive but both sites proved hydridic enough to undergo the abstraction reaction (Scheme 58).



Scheme 58. Hydride abstraction from a CAAC-gold(I) alkyl complex.

6. Summary and Outlook

Except a few notable contributions from the 1970s, the reactivity of gold complexes has been very scarcely investigated and it remained for a long time limited to Lewis acid behavior. But significant progress has been achieved recently. A series of fundamental organometallic studies has shown that the reactivity of gold complexes is in fact versatile and goes well beyond π-activation. Direct evidence for oxidative addition, reductive elimination, transmetallation, and migratory insertion has been reported, demonstrating the ability of gold to undergo the major elementary steps of organometallic chemistry.

But as shown in this Review, the factors governing the reactivity of gold complexes do not systematically parallel those of the other transition metals, especially of the neighboring Group 10 metals. Gold has peculiar coordination properties and its coordination environment plays a major role in reactivity, for both gold(I) and gold(III) complexes. The design of appropriate ligands and the preparation of suitable complexes is thus critical.

If the reactivity of gold complexes has been significantly expanded, the field is still in its infancy and much remains to be done before our knowledge on gold reaches that of the Group 10 metals. Some of the elementary reactions (migratory insertion, oxidative addition) have been only recently substantiated and their scope is still relatively limited. Other transformations, such as β-hydride/halide/alkyl eliminations, are hitherto unknown. An important challenge will also consist in the development of viable catalytic cycles based on these elementary steps.[12,22,120,121]

It is not the aim to simply reproduce the known Pd-catalyzed transformations with gold complexes, and future research should take advantage of the specific properties of gold (in particular its unique functional group tolerance and Lewis acidity) to develop synthetically useful transformations. Accordingly, milder conditions, broader substrate scope, unusual selectivity may be achieved, new transformations may also be discovered.

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[1] H. Schmidbaur, *Naturwiss. Rundsch.* **1995**, *48*, 443–451.
[2] a) Y. Fukuda, K. Utimoto, *J. Org. Chem.* **1991**, *56*, 3729–3731; b) J. H. Teles, S. Brode, M. Chabanas, *Angew. Chem. Int. Ed.* **1998**, *37*, 1415–1418; *Angew. Chem.* **1998**, *110*, 1475–1478; c) A. S. K. Hashmi, L. Schwarz, J. H. Choi, T. M. Frost, *Angew. Chem. Int. Ed.* **2000**, *39*, 2285–2288; *Angew. Chem.* **2000**, *112*, 2382–2385; d) A. S. K. Hashmi, T. M. Frost, J. W. Bats, *J. Am. Chem. Soc.* **2000**, *122*, 11553–11554.
[3] For Reviews on gold catalysis, see: a) A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.* **2006**, *45*, 7896–7936; *Angew. Chem.* **2006**, *118*, 8064–8105; b) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; c) A. Fürstner, P. W. Davies, *Angew. Chem. Int. Ed.* **2007**, *46*, 3410–3449; *Angew. Chem.* **2007**, *119*, 3478–3519; d) A. Arcadi, *Chem. Rev.* **2008**, *108*, 3266–3325; e) E. Jiménez-Núnez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; f) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378; g) A. Fürstner, *Chem. Soc. Rev.* **2009**, *38*, 3208–3221; h) A. Corma, A. Leyva-Perez, M. J. Sabater, *Chem. Rev.* **2011**, *111*, 1657–1712; i) M. Rudolph, A. S. K. Hashmi, *Chem. Soc. Rev.* **2012**, *41*, 2448–2462.
[4] For a recent Review on dual gold catalysis, see: A. S. K. Hashmi, *Acc. Chem. Res.* **2014**, *47*, 864–876.

[5] a) A. S. K. Hashmi, D. F. Toste, *Modern Gold Catalyzed Synthesis*, Wiley-VCH, Weinheim, **2012**; b) R. Dorel, A. M. Echavarren, *Chem. Rev.* **2015**, *115*, 9028 – 9072.

[6] For Reviews on catalytic intermediates in gold catalysis, see: a) A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2010**, *49*, 5232 – 5241; *Angew. Chem.* **2010**, *122*, 5360 – 5369; b) L. P. Liu, G. B. Hammond, *Chem. Soc. Rev.* **2012**, *41*, 3129 – 3139; c) A. M. Echavarren, C. Obradors, *Chem. Commun.* **2014**, *50*, 16 – 28.

[7] For Reviews on π-complexes, see: a) H. Schmidbaur, A. Schier, *Organometallics* **2010**, *29*, 2 – 23; b) R. E. M. Brooner, R. A. Widenhoefer, *Angew. Chem. Int. Ed.* **2013**, *52*, 11714 – 11724; *Angew. Chem.* **2013**, *125*, 11930 – 11941.

[8] For isolation of σ, π-diaurated complexes, see: a) A. Gómez-Suárez, S. Dupuy, A. M. Z. Slawin, S. P. Nolan, *Angew. Chem. Int. Ed.* **2013**, *52*, 938 – 942; *Angew. Chem.* **2013**, *125*, 972 – 976; b) D. Weber, M. R. Gagné, *Chem. Sci.* **2013**, *4*, 335 – 338; c) A. S. K. Hashmi, T. Lauterbach, P. Nösel, M. H. Vilhelmsen, M. Rudolph, F. Rominger, *Chem. Eur. J.* **2013**, *19*, 1058 – 1065.

[9] For Reviews on carbene/carbenoid/carbocation species, see: a) H. G. Raubenheimer, S. Cronje, *Chem. Soc. Rev.* **2008**, *37*, 1998 – 2011; b) A. M. Echavarren, *Nat. Chem.* **2009**, *1*, 431 – 433; c) D. Benitez, N. D. Shapiro, E. Tkatchouk, Y. Wang, W. A. Goddard III, F. D. Toste, *Nat. Chem.* **2009**, *1*, 482 – 486; d) Y. Wang, M. E. Muratore, A. M. Echavarren, *Chem. Eur. J.* **2015**, *21*, 7332 – 7339; e) D. Qian, J. Zhang, *Chem. Soc. Rev.* **2015**, *44*, 677 – 698.

[10] J. F. Hartwig, *Organotransition Metal Chemistry*: *From Bonding to Catalysis*, University Science Books, Sausalito, **2009**.

[11] For recent Reviews, see: a) M. N. Hopkinson, A. D. Gee, V. Gouverneur, *Chem. Eur. J.* **2011**, *17*, 8248 – 8262; b) P. Garcia, M. Malacria, C. Aubert, V. Gandon, L. Fensterbank, *ChemCatChem* **2010**, *2*, 493 – 497; c) H. A. Wegner, M. Auzias, *Angew. Chem. Int. Ed.* **2011**, *50*, 8236 – 8247; *Angew. Chem.* **2011**, *123*, 8386 – 8397; d) T. C. Boorman, I. Larrosa, *Chem. Soc. Rev.* **2011**, *40*, 1910 – 1925.

[12] Very recently, alternative strategies to achieve $\mathrm{Au^I/Au^{III}}$ catalytic cycles have been developed using aryldiazonium or aryliodonium species, see: a) B. Sahoo, M. N. Hopkinson, F. Glorius, *J. Am. Chem. Soc.* **2013**, *135*, 5505 – 5508; b) X.-Z. Shu, M. Zhang, Y. He, H. Frei, F. D. Toste, *J. Am. Chem. Soc.* **2014**, *136*, 5844 – 5847; c) R. Cai, M. Lu, E. Y. Aguilera, Y. Xi, N. G. Akhmedov, J. L. Petersen, H. Chen, X. Shi, *Angew. Chem. Int. Ed.* **2015**, *54*, 8772 – 8776; *Angew. Chem.* **2015**, *127*, 8896 – 8900.

[13] D. J. Gorin, F. D. Toste, *Nature* **2007**, *446*, 395 – 403.

[14] a) T. Lauterbach, M. Livendahl, A. Rosellón, P. Espinet, A. M. Echavarren, *Org. Lett.* **2010**, *12*, 3006 – 3009; b) M. Livendahl, P. Espinet, A. M. Echavarren, *Platinum Met. Rev.* **2011**, *55*, 212 – 214.

[15] A. S. K. Hashmi, C. Lothschütz, R. Döpp, M. Ackermann, J. D. B. Becker, M. Rudolph, C. Scholz, F. Rominger, *Adv. Synth. Catal.* **2012**, *354*, 133 – 147.

[16] The standard electrode potentials for $\mathrm{Au^{3+}/Au^{+}}$ and $\mathrm{Pd^{2+}/Pd^{0}}$ in aqueous solution are 1.41 and 0.94 V, respectively. See S. G. Bratsch, *J. Phys. Chem. Ref. Data* **1989**, *18*, 1 – 21.

[17] J. H. Teles, *Angew. Chem. Int. Ed.* **2015**, *54*, 5556 – 5558; *Angew. Chem.* **2015**, *127*, 5648 – 5650.

[18] A. Tamaki, J. K. Kochi, *J. Organomet. Chem.* **1972**, *40*, C81 – C84.

[19] A. Shiotani, H. Schmidbaur, *J. Organomet. Chem.* **1972**, *37*, C24 – C26.

[20] a) A. Johnson, R.. Puddephatt, *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 1175 – 1177; b) A. Johnson, R. J. Puddephatt, *J. Organomet. Chem.* **1975**, *85*, 115 – 121.

[21] M. T. Johnson, J. M. J. van Rensburg, M. Axelsson, M. S. G. Ahlquist, O. F. Wendt, *Chem. Sci.* **2011**, *2*, 2373 – 2377.

[22] M. D. Levin, F. D. Toste, *Angew. Chem. Int. Ed.* **2014**, *53*, 6211 – 6215; *Angew. Chem.* **2014**, *126*, 6325 – 6329.

[23] Bimetallic complexes of the general formula $\mathrm{[Au(R_2PCH_2)_2]_2}$ were shown by Schmidbaur and Fackler to react with methyl iodide within minutes at 25 °C, affording the corresponding formal $\mathrm{Au^{II}}$–$\mathrm{Au^{II}}$ and $\mathrm{Au^{III}}$–$\mathrm{Au^{III}}$ complexes, depending on the employed stoichiometry of MeI. The reactions proceed via $\mathrm{S_N2}$-type mechanisms and are facilitated by the two proximal metal centers. See: a) A. Laguna, M. Laguna, *Coord. Chem. Rev.* **1999**, *193 – 195*, 837 – 856; b) J. P. Fackler, *Inorg. Chem.* **2002**, *41*, 6959 – 6972; c) P. Jandik, U. Schubert, H. Schmidbaur, *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 73; *Angew. Chem.* **1982**, *94*, 74 – 75.

[24] K. L. Vikse, A. Zavras, T. H. Thomas, A. Ariafard, G. N. Khairallah, A. J. Canty, B. F. Yates, R. A. J. O'Hair, *Organometallics* **2015**, *34*, 3255 – 3263.

[25] M. S. Winston, W. J. Wolf, F. D. Toste, *J. Am. Chem. Soc.* **2014**, *136*, 7777 – 7782.

[26] C. González-Arellano, A. Corma, M. Iglesias, F. Sánchez, *J. Catal.* **2006**, *238*, 497 – 501.

[27] C. González-Arellano, A. Abad, A. Corma, H. García, M. Iglesias, F. Sánchez, *Angew. Chem. Int. Ed.* **2007**, *46*, 1536 – 1538; *Angew. Chem.* **2007**, *119*, 1558 – 1560.

[28] The catalytic activity was proposed to result from palladium impurities at low ppm levels, see Ref. [14] and *Chem. Eng. News* **2011**, *89*, 30 – 31.

[29] A. Corma, R. Juárez, M. Boronat, F. Sánchez, M. Iglesias, H. García, *Chem. Commun.* **2011**, *47*, 1446 – 1448.

[30] For a recent Review on the catalytic activity of these subnanometric gold species, see: M. Boronat, A. Leyva-Pérez, A. Corma, *Acc. Chem. Res.* **2014**, *47*, 834 – 844.

[31] P. S. D. Robinson, G. N. Khairallah, G. da Silva, H. Lioe, R. A. J. O'Hair, *Angew. Chem. Int. Ed.* **2012**, *51*, 3812 – 3817; *Angew. Chem.* **2012**, *124*, 3878 – 3883.

[32] R. E. Bachman, S. A. Bodolosky-Bettis, C. J. Pyle, M. A. Gray, *J. Am. Chem. Soc.* **2008**, *130*, 14303 – 14310.

[33] Early on Davison and Ibers reported the oxidative addition of bis(trifluoromethyl)-1,2-dithioethane to $\mathrm{(Ph_3P)AuCl}$ yielding a chlorotriphenylphosphonium tetrathiolatoaurate(III) salt. See: a) A. Davison, D. V. Howe, E. T. Shawl, *Inorg. Chem.* **1967**, *6*, 458 – 463; b) J. H. Enemark, J. A. Ibers, *Inorg. Chem.* **1968**, *7*, 2636 – 2642.

[34] P. Gualco, S. Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2011**, *50*, 8320 – 8324; *Angew. Chem.* **2011**, *123*, 8470 – 8474.

[35] The bis(silyl)gold(III) complex featuring a chloride anion is not stable above −60 °C. It reacts with water or oxygen to give a diphosphine gold(I) complex featuring a net insertion of an oxygen atom in the Si–Si bond. This sequence presents a rare example of a gold(I) – gold(III) – gold(I) redox process. See: P. Gualco, S. Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *Organometallics* **2012**, *31*, 6001 – 6004.

[36] N. Lassauque, P. Gualco, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2013**, *135*, 13827 – 13834.

[37] Upon coordination to copper, a very rare σ-complex has been isolated and structurally characterized, see: P. Gualco, A. Amgoune, K. Miqueu, S. Ladeira, D. Bourissou, *J. Am. Chem. Soc.* **2011**, *133*, 4257 – 4259.

[38] J. Guenther, S. Mallet-Ladeira, L. Estevez, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2014**, *136*, 1778 – 1781.

[39] A. M. Echavarren, M. Livendahl, C. Goehry, F. Maseras, *Chem. Commun.* **2014**, *50*, 1533 – 1536.

[40] M. A. Carvajal, J. J. Novoa, S. Alvarez, *J. Am. Chem. Soc.* **2004**, *126*, 1465 – 1477.

[41] M. Joost, P. Gualco, Y. Coppel, K. Miqueu, C. E. Kefalidis, L. Maron, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2014**, *53*, 747 – 751; *Angew. Chem.* **2014**, *126*, 766 – 770.

[42] C.-Y. Wu, T. Horibe, C. B. Jacobsen, F. D. Toste, *Nature* **2015**, *517*, 449 – 454.

[43] K. Ruhland, *Eur. J. Org. Chem.* **2012**, 2683 – 2706.

[44] W. D. Jones in *C–C Bond Activation* (Ed.: G. Dong), Springer, Berlin, Heidelberg, **2013**, pp. 1 – 31.

[45] For a Review on the influence of the bite angle of bidentate ligands, see: P. W. N. M. van Leeuwen, P. C. J. Kamer, J. N. H. Reek, P. Dierkes, *Chem. Rev.* **2000**, *100*, 2741 – 2770.

[46] The influence of the bite angle of bidentate ligands on the nature and the energy levels of the frontier molecular orbitals was highlighted early on for oxidative additions to Pd and Pt complexes. See: a) S. Otsuka, *J. Organomet. Chem.* **1980**, *200*, 191 – 205; b) P. Hofmann, H. Heiß, G. Müller, *Z. Naturforsch. B* **1987**, *42*, 395 – 409. For more recent discussions, see also: c) W. Nakanishi, M. Yamanaka, E. Nakamura, *J. Am. Chem. Soc.* **2005**, *127*, 1446; d) N. Yoshikai, E. Nakamura, *Chem. Rev.* **2012**, *112*, 2339.

[47] a) H. Schmidbaur, *Gold Bull.* **2000**, *33*, 3 – 10; b) H. Schmidbaur, *Nature* **2001**, *413*, 31 – 33.

[48] H. Schmidbaur, A. Schier, *Chem. Soc. Rev.* **2012**, *41*, 370 – 412.

[49] M. C. Gimeno, A. Laguna, *Chem. Rev.* **1997**, *97*, 511 – 522.

[50] O. Crespo, M. C. Gimeno, A. Laguna, P. G. Jones, *J. Chem. Soc. Dalton Trans.* **1992**, 1601 – 1605.

[51] M. Joost, A. Zeineddine, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2014**, *136*, 14654 – 14657.

[52] Zhang proposed a $2e^-$ redox sequence to account for the gold(I)-catalyzed dehydrofluorination of perfluoroarenes and according to DFT calculations, the rate-determining step would be the oxidative addition of the $C(sp^2)-F$ bond to the $[(Xantphos)Au]^+$ complex (PAuP = 152°, $\Delta E^{\neq} \approx 30$ kcal mol^{-1}). See: J.-H. Zhan, H. Lv, Y. Yu, J.-L. Zhang, *Adv. Synth. Catal.* **2012**, *354*, 1529 – 1541.

[53] I. Fernández, L. P. Wolters, F. M. Bickelhaupt, *J. Comput. Chem.* **2014**, *35*, 2140 – 2145.

[54] M. Joost, L. Estévez, K. Miqueu, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2015**, *54*, 5236 – 5240; *Angew. Chem.* **2015**, *127*, 5325 – 5329.

[55] For selected Reviews discussing the importance of relativistic effects on the intrinsic properties of gold complexes, see: a) P. Pyykkö, *Angew. Chem. Int. Ed.* **2004**, *43*, 4412 – 4456; *Angew. Chem.* **2004**, *116*, 4512 – 4557; b) P. Pyykkö, *Chem. Soc. Rev.* **2008**, *37*, 1967 – 1997; c) A. Leyva-Pérez, A. Corma, *Angew. Chem. Int. Ed.* **2012**, *51*, 614 – 635; *Angew. Chem.* **2012**, *124*, 636 – 658, and Ref. [3c,13].

[56] The strength of L–Au bonds in $[L_2Au]^+$ and LAuCl complexes ($L = R_3P$) has been quantified computationally and shown to be significantly enhanced by relativistic effects. See: G. A. Bowmaker, H. Schmidbaur, S. Krüger, N. Rösch, *Inorg. Chem.* **1997**, *36*, 1754 – 1757.

[57] P. Schwerdtfeger, H. L. Hermann, H. Schmidbaur, *Inorg. Chem.* **2003**, *42*, 1334 – 1342.

[58] F. H. Brain, C. S. Gibson, *J. Chem. Soc. Resumed* **1939**, 762 – 767.

[59] M. Aresta, G. Vasapollo, *J. Organomet. Chem.* **1973**, *50*, C51 – C53.

[60] Similar aryl halide formations were observed as well upon reaction of perhalophenyl phosphine or arsine gold(I) complexes with dihalogens (Cl_2, Br_2, I_2), although the supposed intermediate gold(III) complexes were not characterized. See: a) R. Usón, A. Laguna, J. Pardo, *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 499 – 513; b) R. Usón, A. Laguna, J. Vicente, *J. Organomet. Chem.* **1975**, *86*, 415 – 421.

[61] A. Tamaki, S. A. Magennis, J. K. Kochi, *J. Am. Chem. Soc.* **1974**, *96*, 6140 – 6148.

[62] S. Komiya, T. A. Albright, R. Hoffmann, J. K. Kochi, *J. Am. Chem. Soc.* **1976**, *98*, 7255 – 7265.

[63] S. Komiya, J. K. Kochi, *J. Am. Chem. Soc.* **1976**, *98*, 7599 – 7607.

[64] Very little is known about three-coordinate gold(III) intermediates. They may adopt T- or Y-shaped geometry, see Ref. [62]. To date, nothing indicates that this influences the reductive elimination process and it is likely that the complexes rapidly isomerize in solution. For sake of consistency, all the three-coordinate gold(III) intermediates will be represented with a Y-shaped geometry.

[65] L. P. Kuch, R. S. Tobias, *J. Organomet. Chem.* **1976**, *122*, 429 – 446.

[66] S. Komiya, A. Shibue, *Organometallics* **1985**, *4*, 684 – 687.

[67] S. Komiya, S. Ozaki, A. Shibue, *J. Chem. Soc. Chem. Commun.* **1986**, 1555 – 1556.

[68] V. J. Scott, J. A. Labinger, J. E. Bercaw, *Organometallics* **2010**, *29*, 4090 – 4096.

[69] N. P. Mankad, F. D. Toste, *Chem. Sci.* **2012**, *3*, 72 – 76.

[70] N. P. Mankad, F. D. Toste, *J. Am. Chem. Soc.* **2010**, *132*, 12859 – 12861.

[71] M. J. Ghidiu, A. J. Pistner, G. P. A. Yap, D. A. Lutterman, J. Rosenthal, *Organometallics* **2013**, *32*, 5026 – 5029.

[72] M. J. Ghidiu, A. J. Pistner, G. P. A. Yap, D. A. Lutterman, J. Rosenthal, *Organometallics* **2013**, *32*, 6628.

[73] The selectivity of the reductive elimination ($C(sp^2)-X$ vs. $C(sp^2)-CF_3$) was recently shown to depend on the nature of the halide, see: M. S. Winston, W. J. Wolf, F. D. Toste, *J. Am. Chem. Soc.* **2015**, *137*, 7921 – 7928.

[74] S. Lavy, J. J. Miller, M. Pažický, A.-S. Rodrigues, F. Rominger, C. Jäkel, D. Serra, N. Vinokurov, M. Limbach, *Adv. Synth. Catal.* **2010**, *352*, 2993 – 3000.

[75] J. Vicente, M. D. Bermúdez, J. Escribano, M. P. Carrillo, P. G. Jones, *J. Chem. Soc. Dalton Trans.* **1990**, 3083.

[76] J. Vicente, M. D. Bermudez, J. Escribano, *Organometallics* **1991**, *10*, 3380 – 3384.

[77] J. Vicente, M. D. Bermúdez, F. J. Carrión, *Inorg. Chim. Acta* **1994**, *220*, 1 – 3.

[78] W. J. Wolf, M. S. Winston, F. D. Toste, *Nat. Chem.* **2014**, *6*, 159 – 164.

[79] A. Nijamudheen, S. Karmakar, A. Datta, *Chem. Eur. J.* **2014**, *20*, 14650 – 14658.

[80] M. Hofer, E. Gomez-Bengoa, C. Nevado, *Organometallics* **2014**, *33*, 1328 – 1332.

[81] M. Contel, M. Stol, M. A. Casado, G. P. M. van Klink, D. D. Ellis, A. L. Spek, G. van Koten, *Organometallics* **2002**, *21*, 4556 – 4559.

[82] Y. Shi, S. M. Peterson, W. W. Haberaecker, S. A. Blum, *J. Am. Chem. Soc.* **2008**, *130*, 2168 – 2169.

[83] J. J. Hirner, Y. Shi, S. A. Blum, *Acc. Chem. Res.* **2011**, *44*, 603 – 613.

[84] D. Serra, M.-E. Moret, P. Chen, *J. Am. Chem. Soc.* **2011**, *133*, 8914 – 8926.

[85] M. H. Pérez-Temprano, J. A. Casares, Á. R. de Lera, R. Álvarez, P. Espinet, *Angew. Chem. Int. Ed.* **2012**, *51*, 4917 – 4920; *Angew. Chem.* **2012**, *124*, 5001 – 5004.

[86] M. H. Pérez-Temprano, J. A. Casares, P. Espinet, *Chem. Eur. J.* **2012**, *18*, 1864 – 1884.

[87] T. P. Cornell, Y. Shi, S. A. Blum, *Organometallics* **2012**, *31*, 5990 – 5993.

[88] M. Al-Amin, K. E. Roth, S. A. Blum, *ACS Catal.* **2013**, 622 – 629.

[89] For recent mechanistic studies on Au-to-Pd transmetallation, see: J. delPozo, D. Carrasco, M. H. Pérez-Temprano, M. García-Melchor, R. Álvarez, J. A. Casares, P. Espinet, *Angew. Chem. Int. Ed.* **2013**, *52*, 2189 – 2193; *Angew. Chem.* **2013**, *125*, 2245 – 2249.

[90] A. Sladek, S. Hofreiter, M. Paul, H. Schmidbaur, *J. Organomet. Chem.* **1995**, *501*, 47 – 51.

[91] J. M. Forward, J. P. Fackler, R. J. Staples, *Organometallics* **1995**, *14*, 4194 – 4198.

[92] S. G. Weber, D. Zahner, F. Rominger, B. F. Straub, *Chem. Commun.* **2012**, *48*, 11325 – 11327.

[93] D. V. Partyka, M. Zeller, A. D. Hunter, T. G. Gray, *Angew. Chem. Int. Ed.* **2006**, *45*, 8188 – 8191; *Angew. Chem.* **2006**, *118*, 8368 – 8371.

[94] D. V. Partyka, M. Zeller, A. D. Hunter, T. G. Gray, *Inorg. Chem.* **2012**, *51*, 8394 – 8401.

[95] H. K. Lenker, T. G. Gray, R. A. Stockland, *Dalton Trans.* **2012**, *41*, 13274 – 13276.

[96] D. V. Partyka, A. J. Esswein, M. Zeller, A. D. Hunter, T. G. Gray, *Organometallics* **2007**, *26*, 3279 – 3282.

[97] D. V. Partyka, J. B. Updegraff, M. Zeller, A. D. Hunter, T. G. Gray, *Organometallics* **2009**, *28*, 1666 – 1674.

[98] L. Gao, M. A. Peay, D. V. Partyka, J. B. Updegraff, T. S. Teets, A. J. Esswein, M. Zeller, A. D. Hunter, T. G. Gray, *Organometallics* **2009**, *28*, 5669 – 5681.

[99] a) A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, *J. Organomet. Chem.* **2009**, *694*, 592 – 597; b) A. S. K. Hashmi, T. D. Ramamurthi, M. H. Todd, A. S. K. Tsang, K. Graf, *Aust. J. Chem.* **2010**, *63*, 1619 – 1626.

[100] D. Y. Melgarejo, G. M. Chiarella, J. P. Fackler, *Acta Crystallogr. Sect. C* **2009**, *65*, m299 – m301.

[101] G. Seidel, C. W. Lehmann, A. Fürstner, *Angew. Chem. Int. Ed.* **2010**, *49*, 8466 – 8470; *Angew. Chem.* **2010**, *122*, 8644 – 8648.

[102] J. E. Heckler, M. Zeller, A. D. Hunter, T. G. Gray, *Angew. Chem. Int. Ed.* **2012**, *51*, 5924 – 5928; *Angew. Chem.* **2012**, *124*, 6026 – 6030.

[103] S. Dupuy, L. Crawford, M. Bühl, A. M. Z. Slawin, S. P. Nolan, *Adv. Synth. Catal.* **2012**, *354*, 2380 – 2386.

[104] D.-A. Roşca, D. A. Smith, M. Bochmann, *Chem. Commun.* **2012**, *48*, 7247 – 7249.

[105] D. A. Smith, D.-A. Roşca, M. Bochmann, *Organometallics* **2012**, *31*, 5998 – 6000.

[106] In contrast to gold(III) chloride complexes, gold(III) fluoride species react with both electron-rich and electron-poor aryl boronic acids to give C–C coupled products directly, see Ref. [70]. However, as discussed in Section 3.3, these reactions were proposed to occur through concerted bimolecular reductive elimination rather than B-to-Au transmetallation.

[107] Q. Wu, C. Du, Y. Huang, Z. Long, X. Liu, F. Song, J. You, *Chem. Sci.* **2015**, *6*, 288 – 293.

[108] The Pd-catalyzed Suzuki – Miyaura coupling of arylboronic acids has been recently extended to C,N-cyclometalated gold(III) chlorides, providing efficient access to a large set of mono- and di-arylated (C,N)-gold(III) complexes. See: A. Maity, A. N. Sulicz, N. Deligonul, M. Zeller, A. D. Hunter, T. G. Gray, *Chem. Sci.* **2015**, *6*, 981 – 986.

[109] F. Rekhroukh, R. Brousses, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2014**, *54*, 1266 – 1269; *Angew. Chem.* **2014**, *126*, 1282 – 1285.

[110] M. M. Hansmann, F. Rominger, M. P. Boone, D. W. Stephan, A. S. K. Hashmi, *Organometallics* **2014**, *33*, 4461 – 4470.

[111] S. Dupuy, A. M. Z. Slawin, S. P. Nolan, *Chem. Eur. J.* **2012**, *18*, 14923 – 14928.

[112] Y. Chen, M. Chen, Y. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 6181 – 6186; *Angew. Chem.* **2012**, *124*, 6285 – 6290.

[113] M. S. Kharasch, H. S. Isbell, *J. Am. Chem. Soc.* **1931**, *53*, 3053 – 3059.

[114] Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239 – 3265.

[115] T. de Haro, C. Nevado, *Synthesis* **2011**, *2011*, 2530 – 2539.

[116] J. Xie, C. Pan, A. Abdukader, C. Zhu, *Chem. Soc. Rev.* **2014**, *43*, 5245 – 5256.

[117] M. Hofer, C. Nevado, *Tetrahedron* **2013**, *69*, 5751 – 5757.

[118] P. Lu, T. C. Boorman, A. M. Z. Slawin, I. Larrosa, *J. Am. Chem. Soc.* **2010**, *132*, 5580 – 5581.

[119] X. C. Cambeiro, T. C. Boorman, P. Lu, I. Larrosa, *Angew. Chem. Int. Ed.* **2013**, *52*, 1781 – 1784; *Angew. Chem.* **2013**, *125*, 1825 – 1828.

[120] L. T. Ball, G. C. Lloyd-Jones, C. A. Russell, *Science* **2012**, *337*, 1644 – 1648.

[121] L. T. Ball, G. C. Lloyd-Jones, C. A. Russell, *J. Am. Chem. Soc.* **2014**, *136*, 254 – 264.

[122] M. Lein, M. Rudolph, A. S. K. Hashmi, P. Schwerdtfeger, *Organometallics* **2010**, *29*, 2206 – 2210.

[123] C. M. Krauter, A. S. K. Hashmi, M. Pernpointner, *ChemCatChem* **2010**, *2*, 1226 – 1230.

[124] R. Casado, M. Contel, M. Laguna, P. Romero, S. Sanz, *J. Am. Chem. Soc.* **2003**, *125*, 11925 – 11935.

[125] E. Mizushima, T. Hayashi, M. Tanaka, *Org. Lett.* **2003**, *5*, 3349 – 3352.

[126] V. Lavallo, G. D. Frey, B. Donnadieu, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2008**, *47*, 5224 – 5228; *Angew. Chem.* **2008**, *120*, 5302 – 5306.

[127] R. Kinjo, B. Donnadieu, G. Bertrand, *Angew. Chem. Int. Ed.* **2011**, *50*, 5560 – 5563; *Angew. Chem.* **2011**, *123*, 5674 – 5677.

[128] K. D. Hesp, M. Stradiotto, *J. Am. Chem. Soc.* **2010**, *132*, 18026 – 18029.

[129] G. Kovács, A. Lledós, G. Ujaque, *Angew. Chem. Int. Ed.* **2011**, *50*, 11147 – 11151; *Angew. Chem.* **2011**, *123*, 11343 – 11347.

[130] N. Nishina, Y. Yamamoto, *Angew. Chem. Int. Ed.* **2006**, *45*, 3314 – 3317; *Angew. Chem.* **2006**, *118*, 3392 – 3395.

[131] N. Nishina, Y. Yamamoto, *Synlett* **2007**, 1767 – 1770.

[132] X. Zeng, M. Soleilhavoup, G. Bertrand, *Org. Lett.* **2009**, *11*, 3166 – 3169.

[133] Z. J. Wang, D. Benitez, E. Tkatchouk, W. A. Goddard III, F. D. Toste, *J. Am. Chem. Soc.* **2010**, *132*, 13064 – 13071.

[134] R. L. LaLonde, J. William, E. Brenzovich, D. Benitez, E. Tkatchouk, K. Kelley, I. I. I. William, A. Goddard, F. D. Toste, *Chem. Sci.* **2010**, *1*, 226 – 233.

[135] A. Zhdanko, M. E. Maier, *Angew. Chem. Int. Ed.* **2014**, *53*, 7760 – 7764; *Angew. Chem.* **2014**, *126*, 7894 – 7898.

[136] M. W. Johnson, S. L. Shevick, F. D. Toste, R. G. Bergman, *Chem. Sci.* **2013**, *4*, 1023 – 1027.

[137] Y. Oonishi, A. Gómez-Suárez, A. R. Martin, S. P. Nolan, *Angew. Chem. Int. Ed.* **2013**, *52*, 9767 – 9771; *Angew. Chem.* **2013**, *125*, 9949 – 9953.

[138] J. A. Akana, K. X. Bhattacharyya, P. Müller, J. P. Sadighi, *J. Am. Chem. Soc.* **2007**, *129*, 7736 – 7737.

[139] E. Y. Tsui, P. Müller, J. P. Sadighi, *Angew. Chem. Int. Ed.* **2008**, *47*, 8937 – 8940; *Angew. Chem.* **2008**, *120*, 9069 – 9072.

[140] G. Klatt, R. Xu, M. Pernpointner, L. Molinari, T. Q. Hung, F. Rominger, A. S. K. Hashmi, H. Köppel, *Chem. Eur. J.* **2013**, *19*, 3954 – 3961.

[141] Recently, Blum and co-workers showed that *syn* carboaurations can be efficiently catalyzed by Pd complexes, see Y. Shi, S. D. Ramgen, S. A. Blum, *Organometallics* **2009**, *28*, 1275 – 1277.

[142] a) M. Joost, P. Gualco, S. Mallet-Ladeira, A. Amgoune, D. Bourissou, *Angew. Chem. Int. Ed.* **2013**, *52*, 7160 – 7163; *Angew. Chem.* **2013**, *125*, 7301 – 7304; b) M. Joost, L. Estévez, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2014**, *136*, 10373 – 10382.

[143] V. Kotzabasaki, I. N. Lykakis, C. Gryparis, A. Psyllaki, E. Vasilikogiannaki, M. Stratakis, *Organometallics* **2013**, *32*, 665 – 672.

[144] C. Gryparis, M. Kidonakis, M. Stratakis, *Org. Lett.* **2013**, *15*, 6038 – 6041.

[145] K. Yamaguchi, Y. Wang, T. Oishi, Y. Kuroda, N. Mizuno, *Angew. Chem. Int. Ed.* **2013**, *52*, 5627 – 5630; *Angew. Chem.* **2013**, *125*, 5737 – 5740.

[146] M. W. Johnson, S. W. Bagley, N. P. Mankad, R. G. Bergman, V. Mascitti, F. D. Toste, *Angew. Chem. Int. Ed.* **2014**, *53*, 4404 – 4407; *Angew. Chem.* **2014**, *126*, 4493 – 4496.

[147] W. Henderson, *Adv. Organomet. Chem.* **2006**, *54*, 207–265.

[148] E. Langseth, M. L. Scheuermann, D. Balcells, W. Kaminsky, K. I. Goldberg, O. Eisenstein, R. H. Heyn, M. Tilset, *Angew. Chem. Int. Ed.* **2013**, *52*, 1660–1663; *Angew. Chem.* **2013**, *125*, 1704–1707.

[149] N. Savjani, D.-A. Roşca, M. Schormann, M. Bochmann, *Angew. Chem. Int. Ed.* **2013**, *52*, 874–877; *Angew. Chem.* **2013**, *125*, 908–911.

[150] D.-A. Rosca, D. A. Smith, D. L. Hughes, M. Bochmann, *Angew. Chem. Int. Ed.* **2012**, *51*, 10643–10646; *Angew. Chem.* **2012**, *124*, 10795–10798.

[151] A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2012**, *51*, 12935–12936; *Angew. Chem.* **2012**, *124*, 13109–13110.

[152] E. Langseth, A. Nova, E. A. Tråseth, F. Rise, S. Øien, R. H. Heyn, M. Tilset, *J. Am. Chem. Soc.* **2014**, *136*, 10104–10115.

[153] M. A. Cinellu, G. Minghetti, F. Cocco, S. Stoccoro, A. Zucca, M. Manassero, *Angew. Chem. Int. Ed.* **2005**, *44*, 6892–6895; *Angew. Chem.* **2005**, *117*, 7052–7055.

[154] β-Hydride eliminations at gold have been occasionally proposed, see: B. Alcaide, P. Almendros, T. M. del Campo, I. Fernández, *Chem. Commun.* **2011**, *47*, 9054.

[155] H. Schmidbaur, H. G. Raubenheimer, L. Dobrzańska, *Chem. Soc. Rev.* **2014**, *43*, 345–380.

[156] G. Ung, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 11388–11391; *Angew. Chem.* **2013**, *125*, 11599–11602.

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