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Ferrocenyl Gold Complexes as Efficient Catalysts

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Dedicated to Prof. M. Dolores Villacampa for her contribution to organometallic and especially to ferrocene chemistry

More than half a century after the discovery of the ferrocene structure in 1951, it remains as a suitable building block in many research areas, including catalysis with the development of key chiral catalysts. On the other hand, gold-mediated catalysis has been raised in recent years, allowing the creation of a great variety of C–C bonds and C-heteroatom bonds. In this context, this review covers the recent advances made with the combination of these two iconic figures in the organometallic chemistry field, since the first gold catalyzed reaction using a ferrocene ligand reported in 1986. The combination of the excellent properties and versatility of this metallocene, has allowed the obtainment of a plethora of ligands for metal catalysis, although their use joined to gold catalysis is still scarcely explored.

1. Introduction

Ferrocene has been extensively used during long time as a versatile intermediate for the construction of more complex skeletons.[1] Its singular properties such as electron density, aromaticity and reversible redox characteristics make this molecule a privileged scaffold. These characteristics together with the easy preparation of new synthetic intermediates, in which one or two cyclopentadienyl rings are able to be substituted with a great variety of organic fragments containing for instance, donor heteroatoms, make the ferrocene core a very suitable building block in many research areas. Hence, the search for new compounds, tuning this structural core looking for special properties, has promoted great efforts in the development of new ferrocenyl ligands in medicine as the Ferrocifen species in preclinical evaluation for breast cancer (a),[2] in catalysis with many important chiral phosphane derivatives such as Josiphos (b) and Xyliphos (c) of great industrial importance,[3] in structural chemistry as the ferrocene derivative (d)[4] or in materials as the bodipy-ferrocene dyads (e) (Figure 1).[5]

Although the ferrocene molecule was discovered in 1950s, its chemistry and the design of unusual structures with unique redox properties are still an interesting challenge in organometallic chemistry. Centered on this topic, our group has pioneered the preparation of a good number of ferrocenyl ligands and the studies of their derivatives as metal complexes from a structural[6] and a biological[7] point of view (Figure 2).

Among the well-studied issues concerning organometallic compounds with excellent catalytic properties, gold complexes have experienced a great development since 1990, with the discovery of the carbophilic properties of these species. Since then, a huge number of pivotal examples have been reported overall centered on the activation π-C–C bonds. During these three decades, gold complexes have become a powerful tool in homogeneous catalysis for the construction of appealing architectures.[8,9]

The properties of ferrocenyl derivatives have made their complexes as excellent catalysts, especially those of palladium

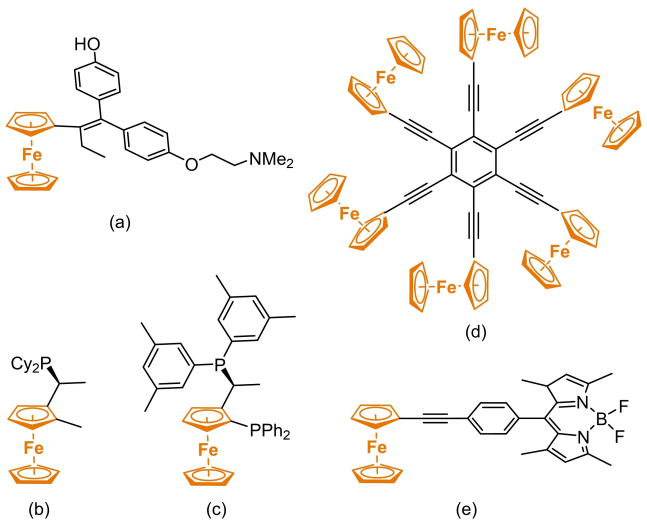

Figure 1. Model examples of ferrocenyl ligands in the different fields of research.

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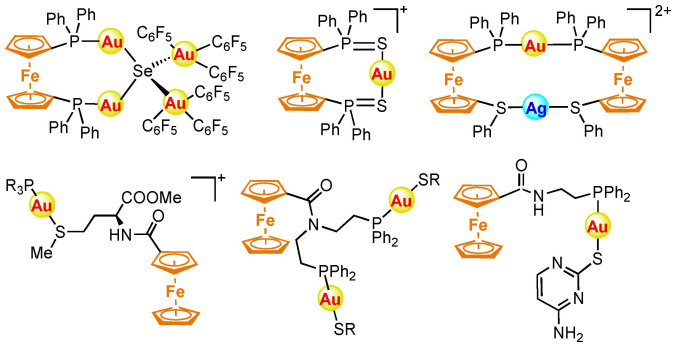

Figure 2. Selected ferrocenyl metal complexes described by us.

which have been well developed.[3b] However, in spite of the great boom of gold catalysis, the presence of the binomial gold-ferrocene is not well studied yet. The great benefits that the ferrocenyl core could provide to the gold catalysts start from: a) the robustness and stability of the ligands, b) the ease functionalization of the metallocene core with several donor atoms and substituents to modulate coordination or steric properties, c) the high conformational flexibility that could vary from rigidity to hemilability, d) the easy access to chiral ferrocenyl ligands, and e) the reversible redox properties of ferrocene that allows the redox-switchable catalysis (RSC).

In this regard, this review will cover a scarce developed topic to date, the ferrocenyl gold complexes used as catalysts.[3] Hence, after the first example of a ferrocenyl gold(I) complex reported by Ito, Hayashi and coworkers in 1986 to catalyze an aldol reaction,[10,11] which represented an important milestone in homogeneous gold catalysis, only scarce examples have been disclosed more recently by other authors using this structural core. Therefore, the main goal of this mini-review is to cover

Juan Carlos Pérez-Sánchez was born in 1999 in Zaragoza (Spain). He graduated in Chemistry with honors ("Bachelor Extraordinary Award") at the University of Zaragoza in 2021. He obtained a Collaboration Fellowship (Spanish Ministry of Education, 2020–2021) in the Inorganic Chemistry Department to work on the project "Pioneering synthesis of chiral metal-organocatalysts derived from ferrocene and study of its applications" and a JAE Intro CSIC Grant (2021–2022) to work on the project "Design and Synthesis of New Molecular Architectures. Study of its Biological and Catalytic Properties", both directed by Prof. M. Concepción Gimeno. He is currently pursuing a Master's degree in Molecular Chemistry and Homogeneous Catalysis at the same university and working on his Master thesis about "Synthesis of Ferrocene based Catalytic Structures and Study of its Properties" under the supervision of Prof. Raquel P. Herrera and Prof. M. Concepción Gimeno at the ISQCH (Spanish Council of Research (CSIC)).

Raquel P. Herrera was born in Alicante (Spain), in 1977. She received her B.Sc. (1999) and M.Sc. degrees (2000) at the University of Alicante, Spain, and completed her Ph.D. (1999–2003) under the supervision of Prof. Guijarro and Prof. Yus at the same university. Then, she took up a European postdoctoral contract with Prof. Ricci (Bologna, Italy) until March 2006, at which time she joined Prof. Lassaletta's and Fernández's group at the IIQ-CSIC (Seville, Spain). She was appointed as a permanent researcher (ARAID program) at the ISQCH-University of Zaragoza in January 2008 and in 2012 she obtained a permanent position as Tenured Scientist of the Spanish Council of Research (CSIC) at the same Institute. Currently she is Scientific Researcher since 2021. In 2012 she was awarded with the Lilly Prize for the best young scientist less than 40 years, in Spain. Her research focuses on asymmetric organocatalysis and its applications. She is the head of the Asymmetric Organocatalysis research group.

M. Concepción Gimeno received her PhD at the University of Zaragoza. After her postdoctoral work with Prof. Stone at the University of Bristol, she joined the Institute of Chemical Synthesis and Homogeneous Catalysis (ISQCH, CSIC-University of Zaragoza), where she is Professor since 2008. Her scientific interests are focused on the design, study and analysis of new group 11 metal compounds with specific catalytic, luminescent and/or biological properties and with potential applications. She is author of more than 280 scientific publications. She has been awarded with the IUPAC 2017 Distinguished Women in Chemistry or Chemical Engineering, the GEQO-Excellence in Organometallic Chemistry Research Award 2017 and RSEQ-Excellence Research Award in 2018, among other awards. She is the head of the Gold and Silver Chemistry research group.

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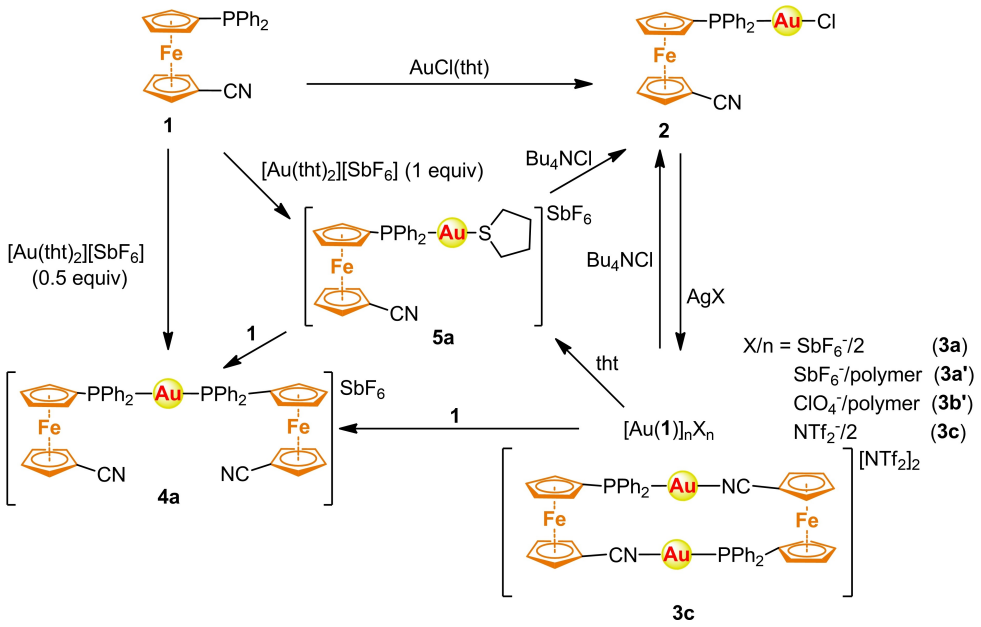


Scheme 1. Synthesis of gold complexes **2**–**5** using 1′-(diphenylphosphanyl)-1-cyanoferrocene (**1**).

these crucial examples and to give to the reader a vision of the work recently done in the literature.[12]

2. Catalytic Properties of Ferrocenyl Gold Complexes

2.1. Ferrocenylphosphane-Gold(I) Complexes

In 2015, Šteˇpnička's group disclosed the synthesis of a series of gold(I) complexes using the ferrocenyl ligand 1′-(diphenylphosphanyl)-1-cyanoferrocene (**1**),[13] as an asymmetric analogue of the widely studied 1,1′-bis(diphenylphosphanyl)ferrocene (dppf).[4a,5b,14] The authors based this idea on their previous developed 1′-(diphenylphosphane)-1-cyanoferrocene copper(I) complexes.[15,16]

The preparation of all gold complexes **2**–**5** with the ferrocenylphosphanylnitrile ligand is shown in Scheme 1.

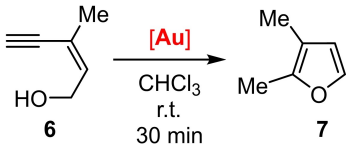
The reaction of ligand **1** with AuCl(tht) (tht = tetrahydrothiophene) occurred rapidly to give complex **2**. The crystal structure of **2** showed the typical linear coordination of gold(I) complexes. In this, neither short contacts between the gold atom and the nitrile groups nor aurophilic interactions were detected.

Complex **2** reacted with silver(I) salts to give cationic complexes of formula $[Au(\mathbf{1})]_nX_n$, where depending on the X anion and the isolation procedure, these compounds have a dimeric structure (**3a** and **3c**) or a polymeric nature (**3a'** and **3b'**) in which both P and N atoms act as bridging ligands giving a zig-zag chain structure.[17]

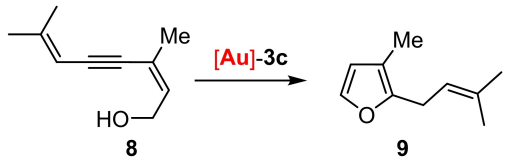
The reaction that gave the formation of complexes **3**, can be reversible by adding $(Bu_4N)Cl$ as a source of chloride. The cleavage of these compounds was also achieved by the addition of ligand **1** or tht. Moreover, the polymer **3a**′ dissolves upon the addition of **1**, giving the mononuclear compound **4a**, where two ligands **1** coordinate through the P atoms to the gold center. The same product could be obtained by treatment of **1** with a half equivalent of $[Au(tht)_2][SbF_6]$. By reaction of **1** with $[Au(tht)_2][SbF_6]$ in a 1:1 molar ratio, complex **4a** was afforded by addition of another equivalent of **1** to the previous formed intermediate **5a**.

The hemilabile nature of the cationic species of Au-**1** is shown by the ability of the phosphane donor moiety, which acts as a firmly bound axis, while neutral and anionic donors can easily cleave the CN–Au bond. This capacity allows generating free coordination vacancies and the possibility of reassembling for a self-stabilization, making these compounds highly attractive in the field of catalysis. In fact, the authors evaluated the catalytic properties of these new complexes with diverse model ring-formation reactions such as those depicted below (Scheme 2–Scheme 4).

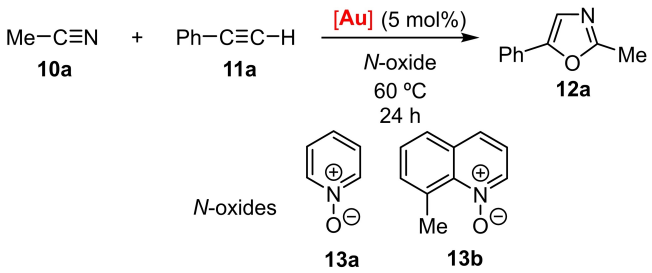
The best results on this reaction were achieved with the complexes **3**, which render full conversions of **6** to **7**. Among them, complex **3c** gave the best results, whose solubility allowed a rapid and complete solution of the catalyst using a catalyst loading of 0.01 mol%. In contrast, complexes **2**, **4a** and



Scheme 2. Cyclization of 2-en-4-yn-1-ol (**6**) to 2,3-dimethyl-furan (**7**).

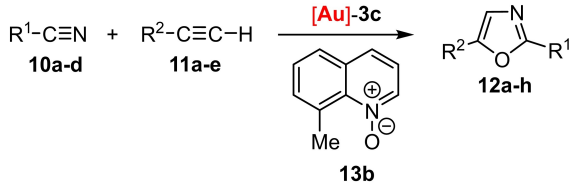


Scheme 3. Gold-catalyzed cycloisomerization of **8** to rosefuran **9**.



Scheme 4. Model gold-catalyzed oxidative cyclization of phenylacetylene **11a** with acetonitrile **10a** to give 1,3-oxazole **12a**.

Table 1. Substrate scope for the oxidative cyclization reaction affording 1,3-oxazoles **12**.[a]



Nitrile	Alkyne	Product	Yield [%]
MeCN (**10a**)	$C_6H_5C\equiv CH$ (**11a**)	**12a**	88
10a	4-$MeC_6H_4C\equiv CH$ (**11b**)	**12b**	92
10a	4-$MeOC_6H_4C\equiv CH$ (**11c**)	**12c**	92
10a	4-$CF_3C_6H_4C\equiv CH$ (**11d**)	**12d**	72
10a	4-$BrC_6H_4C\equiv CH$ (**11e**)	**12e**	82
EtCN (**10b**)	**11a**	**12f**	85
CH_2=CHCN (**10c**)	**11a**	**12g**	46
PhCN (**10d**)[b]	**11a**	**12h**	73

[a] Conditions: alkyne, catalyst **3c**, and **13b** (1.3 equiv.) were reacted in neat nitrile at 60 °C for 24 h. Isolated yields are given as the average of two independent experiments. [b] Reaction with the nitrile (6 equiv.) in chlorobenzene (2 mL).

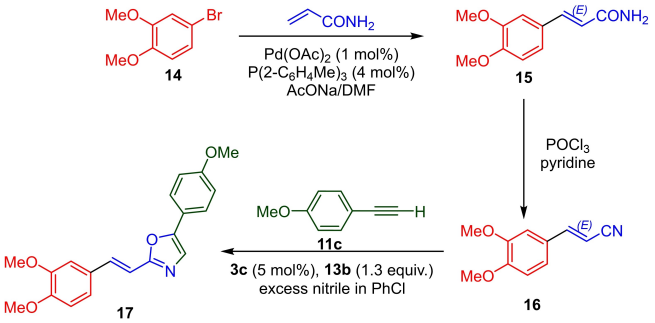
5a were less efficient at the same catalyst loading. A similar annulation reaction was carried out to give rosefuran **9**, a constituent of natural essential oils (Scheme 3).

In this case, the conditions required to promote the catalytic process were stronger, maybe due to the lower reactivity of the internal triple bond of the substrate. Hence, a catalytic amount of 0.5 mol% during 2 h at 60 °C, gave rise to pure rosefuran **9** in 91% yield.

In the same work, all synthesized complexes were tested in a first reaction to prepare the 1,3-oxazole **12a** by a gold-mediated oxidative cyclization of phenylacetylene **11a** with acetonitrile **10a** in the presence of *N*-heterocyclic *N*-oxides **13a** and **13b** (Scheme 4).

Complexes **2**, **4a** and **5a**, as well as the precursor AuCl(tht), gave **12a** with poor yields, which is attributable to coordinatively saturated gold centers in these complexes. In contrast, complexes **3** were more efficient and provided higher yields. Similar to the previous assays, the best results were achieved with the dimer **3c**, which rendered **12a** with a 78% yield using **13a** and 88% yield using **13b**. The scope of the reaction was further tested with different substrates (Table 1), using **3c** and **13b** in acetonitrile, leading to the respective 2,5-disubstituted 1,3-oxazoles **12a–h** in very good isolated yields.

Encouraged by these successful results, a [2+2+1] annulation was also performed in order to prepare the oxazole alkaloid annuloline **17** (Scheme 5). The nitrile precursor **16** was obtained in a two steps reaction through a Pd-catalyzed Heck coupling of 4-bromoveratrole (**14**) with acrylamide followed by a dehydration to form the nitrile (*E*)-**16**. The last step led to a 90:10 mixture of (*E*) and (*Z*) isomers; the unwanted latter isomer was easily removed by recrystallization from ethyl acetate/heptane. The subsequent cyclization of **16** with **11c** and using *N*-oxide **13b** was carried out in chlorobenzene with 5 mol% of **3c** as catalyst, at 60 °C for 24 h. The reaction provided pure **17** in 63% yield after column chromatography. Although the overall yield

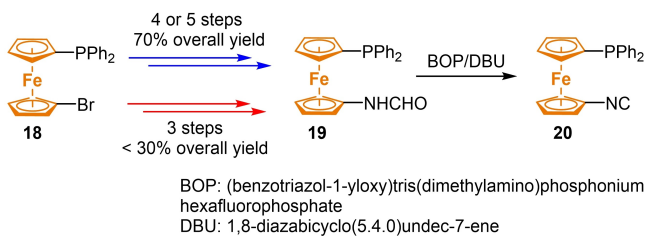


Scheme 5. Synthesis of annuloline **17** by a final Au-mediated cyclization.

toward annuloline **17** of this four-step synthesis is about 34% with respect to **14**.

Later, the same research group continued their studies on the synthesis of cyano-phosphane ferrocene ligands, expanding their possibilities to an isocyanide isomer analogous **20** (Scheme 6).[18,19] Although the structures only differ on the change of the cyano for the isocyanide group, its reactivity and coordination properties are quite different.

Multiple synthetic alternatives were explored starting from 1,1′-dibromoferrocene or from 1′-diphenylphosphane-1-bromoferrocene **18** towards 1′-(diphenylphosphane)-1-



Scheme 6. Synthesis of ferrocenylphosphane isocyanide ligand **20**.

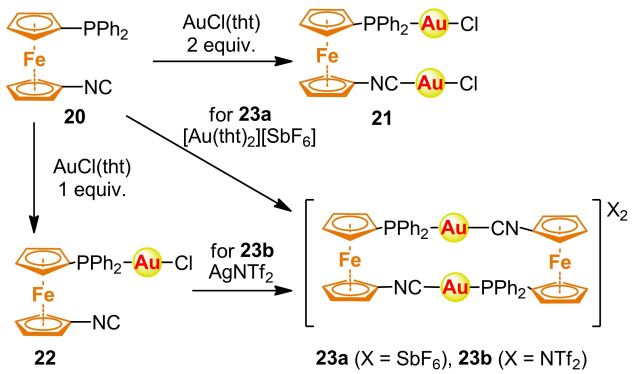
aminoferrocene.[18,19] Once the amine was synthesized, two last steps of formylation and final dehydration of the formamide **19** afforded the desired isonitrile **20**.

With ligand **20** in hand, its reactivity with different gold(I) salts was studied in order to evaluate its coordination properties (Scheme 7).

The reaction with one equivalent of AuCl(tht) afforded the expected linear coordinated phosphane-gold complex [AuCl(**1**-κ*P*)] **22**, while the reaction with two equivalents of AuCl(tht) gave the di-gold complex **21**. The addition of one equivalent of $[Au(tht)_2][SbF_6]$ or the abstraction of chloride ion with $AgNTf_2$ led to the dimeric complexes **23 a** or **23 b**, respectively, which could be compared with the structures previously obtained **3**.

In order to evaluate the catalytic properties of these two structural analogues, they were tested in the model cycloisomerization reaction of enynol **6** to 2,3-dimethylfurane **7** described in Scheme 2. Among them, the best results were obtained with 1 mol% of pre-catalyst **21**. However, if we compare the results previously obtained with catalysts **3 c** and its analogues **23 b**, the hemilabile nitrile ligand **3** led to higher yield for catalytic loads 10 or 100 times lower. The lower catalytic activity shown by **23 b** can be associated with a stronger coordination of the gold atom to the RNC fragment, which prevents the dissociation of the bond and the possible formation of coordination vacancies in the metal center. DFT studies confirmed a difference of approximately 12 kcal·mol^{-1} more endergonic for the dissociation of the RNC–Au bond versus the RCN–Au bond, to give the monomeric species $[Au(L)]^+$.

Recently, Štěpnička and co-workers continued their research in order to evaluate the effects that phosphane-type ligands, fc-PR_2, could generate on the catalytic activity of the new dimer



Scheme 7. Synthesis of gold complexes **21**–**23**.

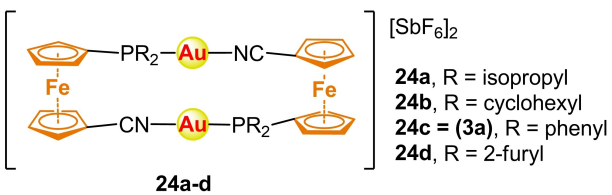


Figure 3. Ferrocenyl gold complexes synthesized **24 a**–**d**.

$[Au_2(\mu\text{-}R_2Pfc'CN)_2][SbF_6]_2$ **24** (fc′ = ferrocene-1,1′-diyl) in comparison with those previously reported (pre-catalysts **3**) (Figure 3).[20]

In order to evaluate their catalytic activity, the cyclization of propargyl amides **25** to oxazolines **26** was chosen to use these dimer complexes **24** as pre-catalysts (Scheme 8). Full conversion was reached in 3 h by all catalysts when used at 1 mol% of catalytic load.

The comparison of the yields obtained for product **26 a**, provided the idea that the activity of alkyl phosphane systems **24 a,b** worked slightly worse than those with an aryl substituent in the phosphane group **24 c,d**. The elaboration of kinetic profiles for this reaction allowed confirming this fact, finding values of rate constants (first order reaction) around 1.6 times higher for the species bearing an aryl-phosphane moiety.

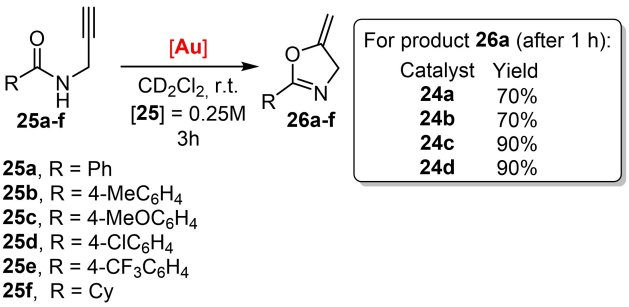
In addition, subsequent studies were carried out with the most active catalyst **24 d** showing that there was no threshold value for the reaction, finding yields (calculated by NMR) of 4% for **26 a** after 90 minutes, with catalytic loads as low as 0.03 mol%.

Štěpnička's group concluded that the presence of weakly σ-donor ligands implied a greater dissociation barrier of dimers **24** ($[Au_2(\mu\text{-}R_2Pfc'CN,\kappa\text{-}P,N)_2]^{2+} \rightarrow 2[Au(fc'\text{-}\kappa P)]^+$). Therefore, the energy of dissociation increases according to **24 b** < **24a** < **24c** < **24d**.

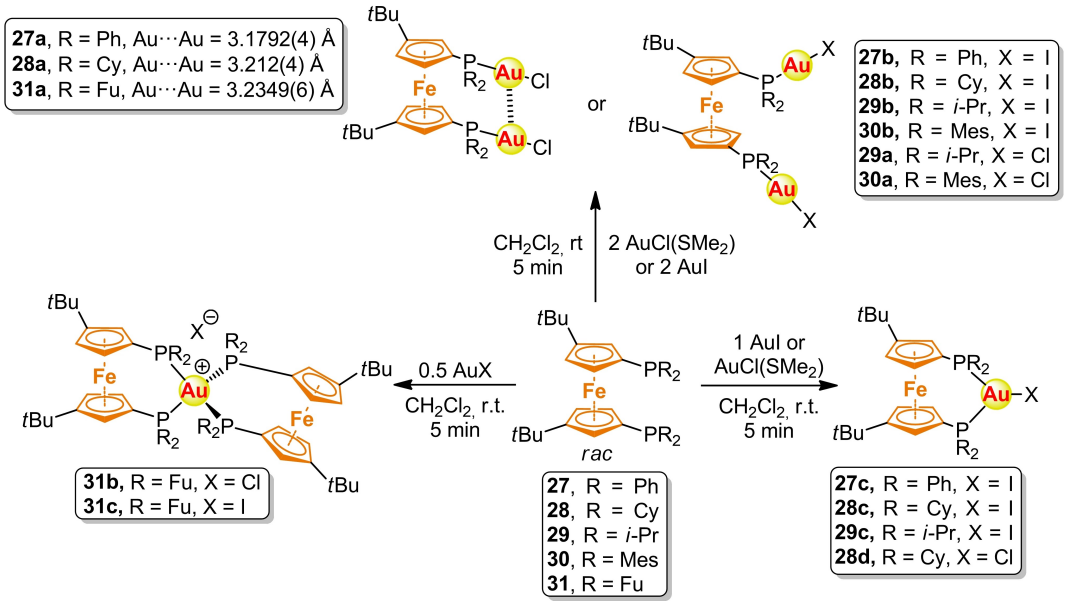
In conclusion, the presence of weakly coordinated nitrile ligands affords the formation of the self-stabilizing species of $[Au_2(\mu\text{-}R_2Pfc'CN,\kappa\text{-}P,N)_2]^{2+}$ whose catalytic activity can be increased through the introduction of phosphane π-acid ligands, fc-PR_2 (lower σ contribution). However, these changes also imply a lower stabilization of $[Au_2(\mu\text{-}R_2Pfc'CN,\kappa\text{-}P,N)_2]^{2+}$ and therefore, it is necessary to find a delicate balance between choosing the phosphane substituents and achieving the greatest catalytic activity.

In 2020, Roger, Hierso and co-workers reported some singular examples of unusual chlorido(iodido)-gold(I) coordination complexes bearing di-*tert*-butyl-bis(phosphane)ferrocene ligands (Scheme 9).[21] The unusual geometries of the final complexes, such as trigonal three-coordinated or tetrahedral four-coordinated, were confirmed by X-ray diffraction techniques.

The introduction of sterically demanding groups like *tert*-butyl ones into the ferrocene moiety favored intramolecular



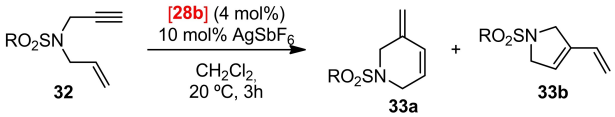
Scheme 8. Gold-catalyzed cyclization of propargyl amides **25 a**–**f** to oxazolines **26 a**–**f**.



Scheme 9. Synthesis of the di-*tert*-butyl-bis(phosphane)ferrocene gold complexes **27**–**31**.

aurophilic interactions (**27a**–**31a**).[22] However, no Au···Au interactions were detected by XRD analysis on the iodide analogues (**28b**–**30b**, **27b** could not be crystallized). In addition, their catalytic properties were evaluated on the cycloaddition of *N*-propargyl-*N*-allyl-4-sulfonylamines **32**. The use of an additional silver salt to activate the pre-catalyst of this reaction was necessary. In fact, in this process, $AgSbF_6$ was the salt of choice. As it is well known, the process consists on the abstraction of the chloride anion from the gold center, giving rise to AgX and interchanging the counteranion of the salt with the metal complex, providing to the real active gold species with a free coordination site. In the preliminary screening experiments, best results were achieved with the linear digold complexes **28a** and **28b**, but no differentiable effect was observed of the iodide derivative compared to chloride complexes. The other tested complexes were less active, probably due to the higher steric congestion of the complexes. As **28b** gave the best conversion, it was selected in order to extend the scope of the reaction, affording to high conversions and selectivities (Table 2).

Table 2. Substrate scope for the cycloaddition of *N*-propargyl-*N*-allyl-4-sulfonylamines **32**.[a]



Entry	R	Conversion in **33a** + **33b** [%]	Selectivity in **33a** [%]
1	C_6H_5 (**32a**)	84	88
2	4-tBu(C_6H_4) (**32b**)	92	86
3	Benzyl (**32c**)	94	88
4	4-F(benzyl) (**32d**)	98	85
5[b]	Me (**32e**)	67	91

[a] Conditions: enynes **32** (0.20 mmol), gold(I) complex **28b** (4 mol%), 2 mL dry CH_2Cl_2 (0.04 M in enyne), 20 °C, 3 h, $AgSbF_6$ (10 mol%). Average conversion from triplicate experiments, isolated yields reported in SI. [b] 1,2-dichloroethane, 60 °C.

2.2. Redox-Switchable Catalysts

The concept of redox-switchable catalysis (RSC),[23] discovered in 1995 by Wrighton and co-workers,[24] is based on the idea of tuning the catalytic activity of a transition metal and, consequently, the resulting metal complexes, by modulating the electron-donating or withdrawing nature of a coordinated ligand. Since ferrocene is a versatile molecule able to exhibit a reversible oxidation process, this unit is often used as the redox-active species in catalysis.

Therefore, Sarkar and co-workers synthesized the first mesoionic carbene-based redox-active gold catalysts **34** (Figure 4).[25,26] These mesoionic carbene-type ligands had a useful characteristic in gold-mediated catalysis, the neutral ferrocenyl form of the ligands behaves like a strong electron donor, while the oxidized system, ferrocenium, acts as a poor-electron donor.

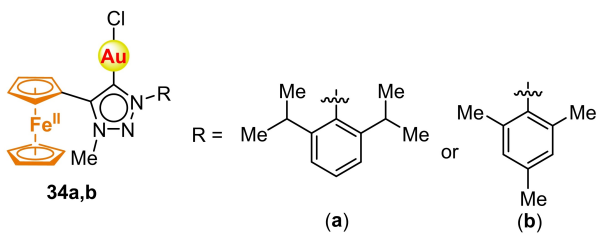


Figure 4. Structure of the mesoionic carbene-based redox-active catalysts **34**.

The singular electronic properties of complexes **34** imply the activation of gold(I) species by oxidation and deactivation by reduction processes, without the use of external salts of silver(I) or copper(II). In order to test this hypothesis of work, the catalytic activity of complex **34b** was explored in the cyclization reaction of *N*-(2-propyn-1-yl)benzamide **25a** to 5-methylene-2-phenyl-4,5-dihydroxazole **26a** using 1 mol% catalyst (Scheme 10).

The pre-catalyst (neutral form) **34b** was *in situ* oxidized by acetylferrocenium tetrafluoroborate to give a ferrocenium form **34b'**, which consequently increased the Lewis acidity of the gold center initiating the catalysis and providing the final product **26a** with good conversion. As a proof of this reactivity, the reaction performed under identical conditions but with the un-oxidized neutral complex **34b** gave no conversion of **26a** after 5 h.

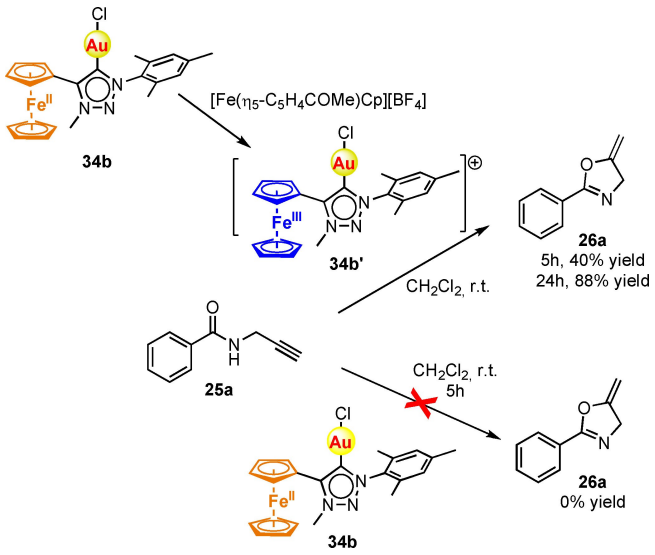
Later, the same research group extended their studies on redox-switchable catalysis for the formation of oxazoline **26**, furan **36** and phenol **38** derivatives by gold(I) catalysis using in this case catalyst **34c** (Scheme 11).[27]

It is expected that the oxidation of the ferrocenyl moiety **34c** to **34c'** increases the Lewis acidity of the gold(I) center making it enough active to induce the catalytic process without any other additive. Moreover, authors studied these gold complexes in three different ring formation reactions. One of them is the cyclization of propargyl amides **25** to oxazolines **26** (Scheme 8). In this sense, in order to evaluate a possible reversible catalytic capacity, a reducing agent $FeCp_2^*$ was chosen by the authors. In this way, the alternate use of an oxidant or a reducing agent allowed to "turn on" or "turn off" the catalytic process. According to the results achieved, in the absence of additives, the maximum conversion was 30% after 24 hours of reaction, while the addition of an oxidant allowed reaching the maximum conversion in 24 h. On the other hand, with an oxidizing additive, after 2.5 h, conversions of 19% were reached, at that time, the reducing agent was added and no noticeable increase in conversion was observed. After 19 h, a new addition of the oxidizing agent rendered a conversion of 75% in 7 h after the catalyst was "turned on".

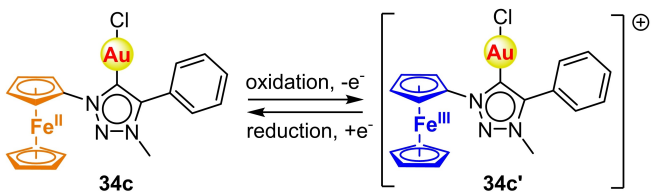
Two more reactions were also evaluated expanding this concept of redox-switchable catalysis. One of them was the cyclization process of 2-methylene-4-phenylbut-3-yn-1-ol (**35**) to 4-methyl-2-phenylfuran (**36**) described in Scheme 12.

In this case, it is observed that in the absence of a catalyst and using exclusively an oxidizing agent did not afford conversion of the final product. However, it was found that after the addition of the oxidant to the pre-catalyst, conversions of 40% were reached in just 45 minutes, although the reaction stopped, and further additions of the oxidant were necessary to achieve a complete conversion. However, the authors could not determine the reason for this observation. The last studied catalytic process was the formation of phenols in a cyclization process of 2-methyl-5-((prop-2-ynyloxy)methyl)furan (**37**) to 4-methyl-1,3-dihydroisobenzofuran-5-ol (**38**) (Scheme 13).

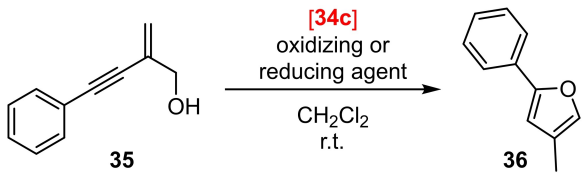
Surprisingly, the formation of phenol **38** was achieved with full conversion within less than 5 min in the presence of ([Fe(η^5-C_5H_4COMe)Cp][BF_4]) to *in situ* generate the oxidized form of the catalyst (complex **34c'**). In contrast, neither the catalysts alone in the absence of an oxidizing agent (24 h, 12%), nor the oxidizing agent by itself rendered good conversion (2.5 h, 0%). Furthermore, the authors observed a very interesting process, the addition of $FeCp_2^*$ allowed the conversion of the product



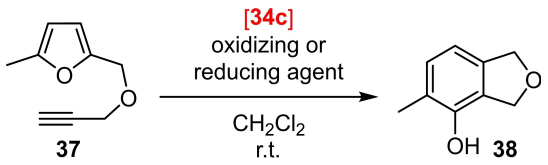
Scheme 10. Gold-catalyzed cyclization of propargyl amides **25a** to 1,3-oxazoline **26a**.



Scheme 11. Structure of redox-switchable catalyst **34c**.



Scheme 12. Gold catalyzed the cyclization process of 2-methylene-4-phenylbut-3-yn-1-ol (**35**) to 4-ethyl-2-phenylfuran (**36**).



Scheme 13. Gold catalyzed cyclization of 2-methyl-5-((prop-2-ynyloxy)methyl)furan (**37**) to 4-methyl-1,3-dihydroisobenzofuran-5-ol (**38**).

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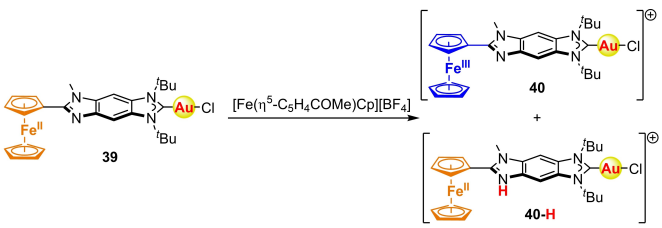
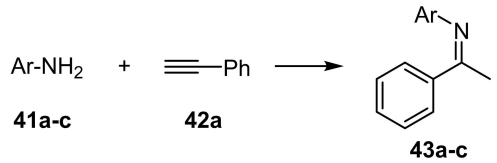
38 back to the original reagent **37**. If [Fe(η^5-C_5H_4COMe)Cp][BF_4] was subsequently added, the phenol **38** was predominantly obtained again, making this process a kind of switching of the reaction *per se*. Later on, Sarkar and Bildstein reported a cationic cobaltocene derivative which was extremely active catalyst without the need of additional oxidants.[28]



Scheme 14. Synthesis of benzo-fused ferrocenyl-imidazolylidene gold(I) complexes **39** and **40**.

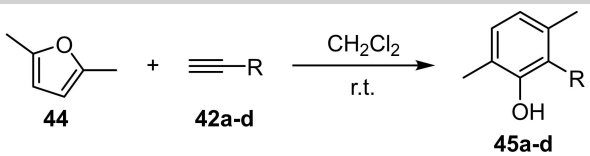
Table 3. Exploration of the hydroamination of terminal alkyne **42a**.[a]



Entry	Ar	Catalyst	Additives[b]	Product	Yield (%)[c]
1	Ph	**39**	$AgBF_4$	**43a**	89
2	Ph	**39**	$AgBF_4$, oxidant	**43a**	91
3	Ph	None	oxidant	**43a**	0
4	4-MeC_6H_4	**39**	$AgBF_4$	**43b**	88
5	4-MeC_6H_4	**39**	$AgBF_4$, oxidant	**43b**	90
6	2,4,6-$Me_3C_6H_2$	**39**	$AgBF_4$	**43c**	82
7	2,4,6-$Me_3C_6H_2$	**39**	$AgBF_4$, oxidant	**43c**	90

[a] Reaction conditions: 0.5 mmol of phenylacetylene **42a**, 0.55 mmol of aryl amine **41**, 1 mol% of the catalyst **39**, 1 mL of CH_3CN at 90 °C, 3 h. [b] 2 mol% of $AgBF_4$ and/or 1 mol% of acetylferrocenium tetrafluoroborate (oxidant) was added to the reaction mixture. [c] Yields were calculated by GC using anisole (0.5 mmol) as internal standard.

Table 4. Study of the cyclization of alkynes **42** with furans **44**.[a]



Entry	R	Catalyst	Product	Yield [%][b]
1	Ph	**39**	**45a**	0
2	Ph	**40** + **40-H**	**45a**	62[c]
3	Ph	**39** + oxidant	**45a**	60[c]
4	1-butyl	**39**	**45b**	0
5	1-butyl	**39** + oxidant	**45b**	53
6	1-hexyl	**39**	**45c**	0
7	1-hexyl	**39** + oxidant	**45c**	66
8	*m*-Tol	**39**	**45d**	0
9	*m*-Tol	**39** + oxidant	**45d**	75

[a] Reaction conditions: 2 mmol of 2,5-dimethylfuran **44**, 1 mmol of alkyne **42**, 0.03 mmol of NaBARF, 3 mol% of the catalyst, 2.5 mL of CH_2Cl_2 at room temperature, 24 h. [b] Isolated yields. [c] Hydroarylated product was also observed.

In 2016, Poyatos, Peris, and co-workers also described a benzo-fused ferrocenyl-imidazolylidene ligand to form gold(I) complex **39** (Scheme 14).[29]

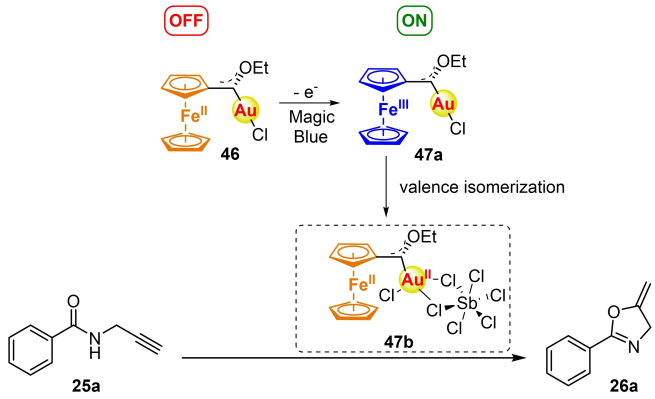
In order to oxidize the ferrocenyl-imidazolylidene complex, it was reacted with acetylferrocenium tetrafluoroborate. The reaction led to a mixture of the ferrocenium complex **40** together with the imidazole-protonated Fe(II) species **40-H**. It was assumed that the ferrocenium moiety increased Lewis acidity of the gold complex giving rise a more active catalyst. This theory was demonstrated in both explored catalytic reactions. The neutral form of the ligand **39** was inert or lead to very low yields, while the oxidized form **40** exhibited an increment in the activity of the gold catalyst. This redox-switchable catalyst was employed in the hydroamination of terminal alkyne **42a** (Table 3) and in the cyclization of alkynes **42** with furans **44** (Table 4). The results of the first reaction are reported in Table 3.[30,31]

The results of the table indicate that there is not a clear increase in the activity of the catalyst when the oxidant is added, since the neutral and the oxidized forms produce very similar results (entries 1 and 2). The authors proposed that this small effect could be due to the fact that the aniline substrate deprotonates the protonated form of the catalyst **40-H** (when it is formed) and thus, regenerates the neutral form **39**. The authors studied a new reaction that did not involve basic substrates in order to evaluate if the presence of the oxidant gave rise a significant improvement (Table 4).

In this case, it can be observed that the neutral form of complex **39** is not active for this reaction. However, the addition of an oxidant renders yields up to 75% (entry 9). In addition, it was used the mixture of complexes **40** and **40-H** (entry 2) obtaining very similar yields to the *in situ* preparation of the oxidized form (entry 3). Therefore, it was demonstrated that the oxidation of the ferrocenyl unit of the complex could act as a switch activating the catalysis. As seen before with other NHC ferrocenyl complexes of gold, this increase in the activity could be the result of an increase in Lewis acidity and electrophilicity of the gold center.

Recently, Heinze and co-workers reported one of the last examples of redox-switchable gold(I) catalysis with a new ferrocene ligand **46** tested on the cyclization of *N*-(2-propyn-1-yl)benzamide **25a** to 2-phenyl-5-vinylidene-2-oxazoline **26a** (Scheme 15).[32]

The authors proposed that oxidation with Magic Blue, [(4-$BrC_6H_4)_3$N]$SbCl_6$, produces the initial Fe(III)/Au(I) that evolves to Fe(II)/Au(II) according to the EPR spectra, and structure **47b** with a tetra-coordinated gold with weakly coordinated chlorido ligands was proposed. The redox-switchable catalyst can reversibly be turned from a very highly active form, in which the coordination of unsaturated gold(II) centers predominates, to an inactive form in which saturated gold(I) centers are coordinated. Interestingly, it was not necessary to add additional Ag(I) or Cu(II) salts to activate the pre-catalyst. However, due to the instability of the cationic gold(II) centers, this must be stabilized by poorly coordinated donor ligands. Apparently, the redox couple Fc^+/Fc acts as a stabilizing system against the



Scheme 15. Ferrocenyl gold(I) catalyzed cyclization of propargyl amide **25a** to oxazoline **26a**.

aggregation or disproportionation of the unsaturated centers of gold(II).

Hey-Hawkins and coworkers prepared interesting trinuclear gold(I) complexes with C3-symmetric trisphosphanes (Figure 5).[33,34] Although the complexes showed scarce values of activity in the absence of oxidant, complex **48a** was finally successful as catalyst in a redox-switchable process, adding different equivalents of 1,1′-diacetylferrocenium tetrakis-(perfluo-*tert*-butoxy)aluminate [fc′Ac$_2$](TEF) as oxidant to switch on the process, and decamethylferrocene as a reductant to turn off the activity of the active species.

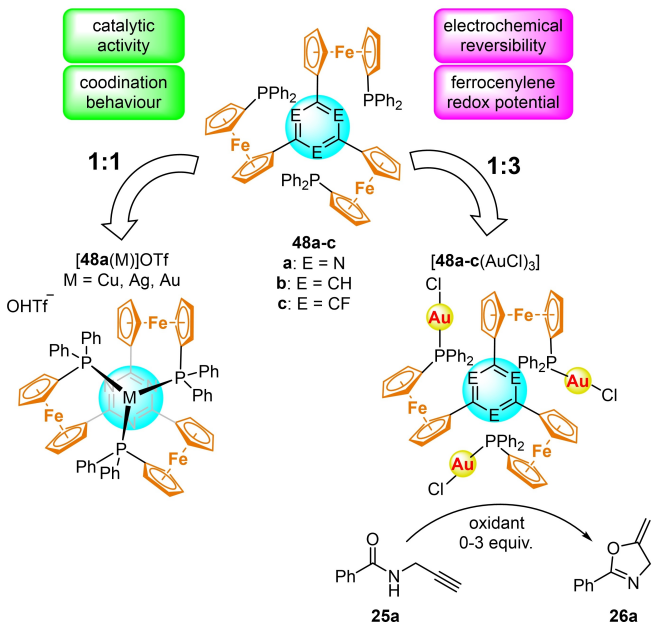


Figure 5. Trinuclear metal complexes with C3-symmetric trisphosphanes **48**.

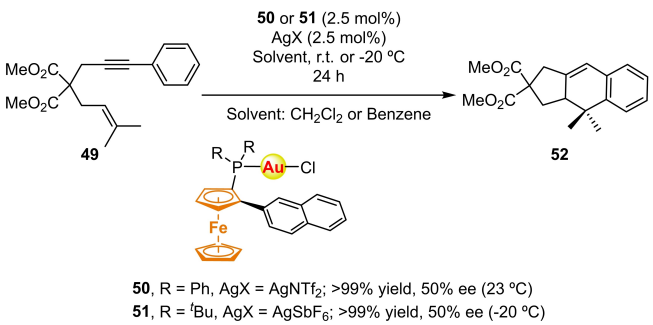
2.3. Chiral Ferrocenylphosphane-Gold(I) Complexes

The preparation and study of chiral ferrocenyl ligands is another relevant topic that deserves some recognition,[35] since the ferrocene structural core gives a relatively easy synthetic access to (planar or helical) chiral ligands, compared to other ligands. However, it is remarkable that the topic regarding gold complexes has been less studied in the literature and the scarce examples are described in this chapter.[36]

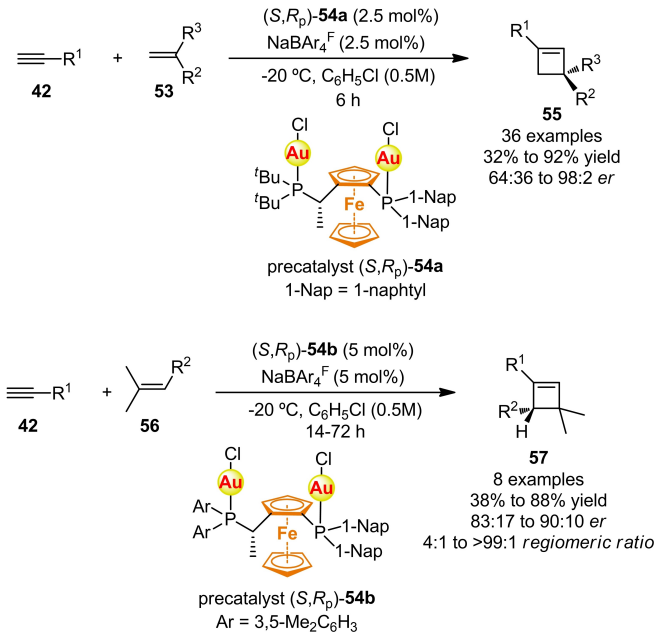
In this field, Echavarren and co-workers reported the first example of a MOPF monophosphane ferrocene gold complex, rarely used in gold asymmetric catalysis before. Although, the best catalytic results of the explored reaction were not achieved with these structures, they deserved special mention (Scheme 16).[37] One of the best results for the enantioselective gold(I) catalyzed [4+2] cycloaddition was obtained by carrying out the reaction in CH_2Cl_2 at −20 °C and $AgSbF_6$ using **51**, giving final adduct in >99% yield and 50% ee.[38]

The same research group, continuing their studies on asymmetric gold catalyzed reactions, described an enantioselective intermolecular gold(I)-catalyzed [2+2] cycloaddition of terminal alkynes and alkenes.[39] This was one of the first examples of an enantioselective synthesis of functionalized cyclobutenes **55** and **57**, using for this aim a large number of non-C_2-chiral digold(I) catalysts derived from Josiphos ligands.[40] After a screening of the process and in order to prove the wide scope of this reaction, different kind of alkynes **42** and 1,1-disubstitued alkenes **53** and **56** were tested using pre-catalysts (S,R_p)-**54a** and (S,R_p)-**54b** (Scheme 17).

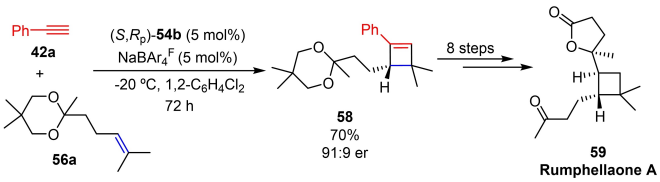
In the first studied process, cyclobutenes **55** were obtained in moderate to excellent yields and enantioselectivities up to 98:2 *er*. Other cycloadditions of trisubstituted alkenes **56** with alkynes **42** were also carried out with another pre-catalyst, (S,R_p)-**54b**, leading to 1,3,3,4-tetrasubstituted cyclobutenes **57** with moderate to excellent regioselectivities and similar enantioselectivities as those obtained with 1,1-disubstitued alkenes **53**. Further, their studies proved that only one of the gold centers was involved in the alkyne activation and the second one was needed in the enantioinduction of the process. Moreover, the utility of this approach was demonstrated in the formal synthesis of rumphellaone A **59**, after 9 reaction steps (Scheme 18),[41] a cytotoxic compound against human T-cell acute lymphoblastic leukemia tumor cells.[42]



Scheme 16. Ferrocenyl gold(I) catalyzed [4+2] cycloaddition reaction.



Scheme 17. Scope of the intermolecular gold(I)-catalyzed [2 + 2] cycloadditions of terminal alkynes **42** and alkenes **53** and **56**.



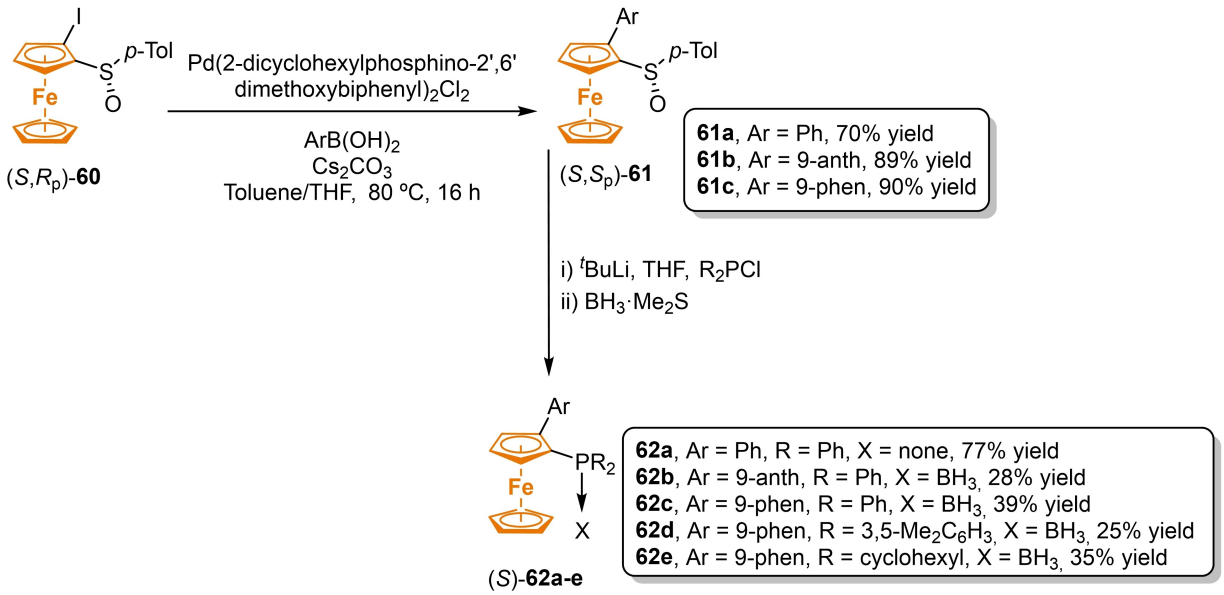
Scheme 18. Formal synthesis of rumphellaone A **59**.

In 2016, Marinetti, Voituriez and co-workers reported a series of MOPF ligands synthesized starting from (*S*,R_p)-1-iodido-2-*p*-tolylsulfinylferrocene (**60**, Scheme 19).[43] Hence, through a Suzuki coupling of (*S*,R_p)-**60** with three different boronic acids, gave three different aromatic systems onto the ferrocenyl moiety **61**. The disubstituted chiral ferrocenyl sulfoxides **61a–c** were obtained in 70–90% yield. The final step of the synthesis afforded different disubstituted ferrocenyl anthracenyl (anth) or phenanthryl (phen) diphosphanes (*S*)-**62a** or their borane adducts (*S*)-**62b–e**, after the addition of ^{t}BuLi to **61**, followed by trapping of the carbanionic ferrocenyl intermediate with a chloridodiaryl- or a chloridodialkylphosphane, respectively (Scheme 19).

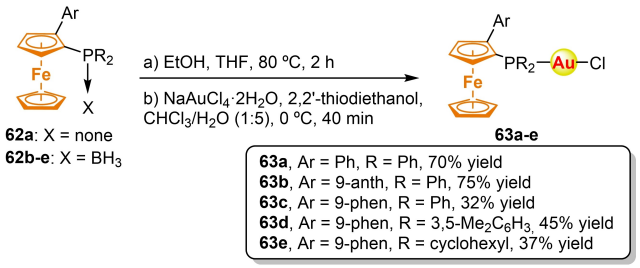
The ensuing synthesis of gold complexes (S)-**63a–e** was carried out in two different ways depending on the nature of the phosphane **62** (Scheme 20). The free phosphane **62a** reacted with AuCl·thiodiethanol, obtained *in situ* by the reaction of $NaAuCl_4 \cdot 2H_2O$ and 2,2′-thiodiethanol, affording (*S*)-**63a** with a yield of 70%. Phosphane boranes (*S*)-**62b–e** were transformed into the corresponding gold complexes (*S*)-**63b–e** by deprotection of the borane (2 h at 80 °C in a THF/EtOH solution), followed by reaction with the same gold precursor at 0 °C.

These complexes were then evaluated in the cycloisomerization of 3-hydroxy-1,5-enynes **64** into bicyclo[3.1.0]hexan-3-ones **65**. Best results were achieved by catalyst **63c** in dichloromethane and AgOTf as the activator salt. With the best reaction conditions in hand, the authors explored the reaction scope as described in Table 5.

The authors have proven the high catalytic activity of these chiral ferrocenyl phosphanes, which can be considered as analogues to the non-chiral Buchwald's phosphane. In addition, their studies showed that the aryl unit of the ferrocenyl moiety induces stabilization towards the cationic gold complex,

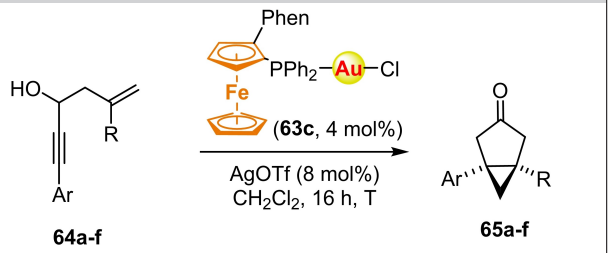


Scheme 19. Synthesis of planar chiral-ferrocenylphosphanes (*S*)-**62a** or their BH_3 complexes (*S*)-**62b–e**.



Scheme 20. Synthesis of gold complexes (*S*)-**63a–e**.

Table 5. Scope of the cycloisomerization of 3-hydroxy-1,5-enynes **64** into bicyclo[3.1.0]hexan-3-ones **65**.



Entry	Substrate	Ar	R	T [°C]	Yield [%]	ee[a] [%]
1	**64a**	Ph	Me	20	85	46
2	**64b**	3,4-Cl_2–C_6H_3	Me	0	87	43
3	**64c**	3-OMe–C_6H_4	Me	0	91	29
4	**64d**	2-OMe–C_6H_4	Me	0	88	20
5	**64e**	4-OMe–C_6H_4	Me	20	67	56
6	**64e**	2-OMe–C_6H_4	Me	0	82	64
7	**64e**	2-OMe–C_6H_4	Me	−40	72	66
8	**64f**	2-OMe–C_6H_4	Ph	0	76	71
9	**64f**	2-OMe–C_6H_4	Ph	−40	79	80

[a] Determined by chiral HPLC.

protecting the metal center, both sterically and electronically, from the reduction to Au^0.

Moreover, these ligands are capable of partially transfer the chirality from the substrate to the products, making these cycloisomerization reactions stereocontrollable in some grade. Consequently, some additional experiments were carried out, comparing catalyst **63c** with its non-chiral arylphosphane ligand analogue and $PtCl_2$. The results obtained showed that the chiral control exerted by the catalyst prevail over the stereocontrol that substrate's stereocenter provides, so the enantioinduction of the reaction is only partial.

3. Conclusions

Gold-mediated catalysis in combination with the use of ferrocenyl ligands is a topic that has been quite unnoticed over the years. With the rapid growth of gold chemistry in the recent years, more and more studies are allowing access to numerous complex and efficient processes employing this metal. The synergy combination of these two scaffolds in catalysis has been reviewed throughout this text, emphasizing the study of three completely different groups of ferrocenyl ligands. The ferrocenyl group can advantageously be used in order to modify the electronic and steric properties of the final gold compounds and, therefore, its reactivity towards catalysis. The tuning of the substituents at one or both Cp rings, the functionalization with different heteroatoms to coordinate the gold center or the use of multidentate species, together with the redox properties or chirality provide an effective way to modulate the coordination properties of gold catalysts bearing ferrocenyl moieties.

Ferrocenyl-phosphane ligands have been extensively studied with other metals; however, their combination with gold metal centers has been less considered. In this context, diphosphane and hemilabile cyanophosphane ferrocenyl ligands are capable of achieving some gold-mediated cyclizations with moderate to high yields and selectivities.

Redox-switchable catalysis has a great potential. The redox pair ferrocene/ferrocenium together with the gold metal center has proven to be an excellent way to modulate the catalytic activity, in a reversible way, as well as avoiding the use of additives, something common for gold catalysts, which mainly act as pre-catalysts. Noticeably, the pair Fe^{III}/Au^{I} can suffer valence isomerization to Fe^{II}/Au^{II} and it seems to have a key role in the catalytic activity.

Finally, the use of chiral ferrocenyl ligands, bearing a carbon stereocenter or with inherent planar chirality has permitted enantioselective transformations, a field that is acquiring special relevance in the gold chemistry field. Moreover, the ferrocene scaffold exhibits quite desirable features to be used as a chiral ligand, such as its rigidity in combination with the bulkiness of the Cp_2Fe backbone or its capacity of offering an additional source of chirality when two substituents are added to the Cp ring (planar chirality). In addition, the donor electronic properties of the ferrocene make its derivatization simple as it reacts faster than benzene in electrophilic aromatic substitution reactions. The scarce examples in the literature have proven that using the ferrocenyl moiety can lead to moderate enantiomeric excesses. However, this topic remains as an undeveloped field, which is still a challenge and can be beneficiated of all the advantages and properties that the ferrocene scaffold could provide.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Ferrocene · Gold · Homogeneous catalysis · Phosphane ligands · Redox chemistry

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