ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Coordination Chemistry Reviews 252 (2008) 1630–1667

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Perfluoroarylgold complexes

Eduardo J. Fernández[a], Antonio Laguna[b,*], M. Elena Olmos[a]

[a] *Departamento de Química, Universidad de la Rioja, Grupo de Síntesis Química de La Rioja, UA-CSIC, Complejo Científico Tecnológico 26001 Logroño, Spain*
[b] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain*

Received 11 October 2007; accepted 28 November 2007
Available online 3 December 2007

Contents

Abstract

The number of arylgold complexes has increased considerably, thanks to the use of perfluoroaryl groups, which confer the compounds a higher thermodynamic and kinetic stability. The present review covers the evolution of the knowledge on perfluoroarylgold chemistry since 1994. It focuses not only on the synthesis and structures, but also on the possible applications, such as those derived from the optical properties. Particular attention has been devoted to homo- or hetero-nuclear compounds displaying intra- or intermolecular metal–metal interactions. The complexes cited in this review are organized attending to the non-aryl ligand/s bonded to gold, going from the simplest ones (halides) to the non-classic ferrocene derivatives or metalloligands.

Keywords: Gold; Perfluoroaryl; Metal–metal interactions; Luminescence

---

* Corresponding author. Tel.: +34 976 761185; fax: +34 976 761187.
E-mail address: alaguna@unizar.es (A. Laguna).

0010-8545/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2007.11.028

1. Introduction

The chemistry of organogold derivatives is an old discipline of organometallic chemistry, being known for almost a century [1,2]. It developed very slowly in the earlier stages – the first review of this field of research was published in 1970 [3] – but has grown considerably in recent decades, as reflected by the number of reviews of organogold chemistry [4–10], although it has only been in the last 20–25 years that practical applications have been found for organogold compounds. Arylgold chemistry is one of the most relevant sub-disciplines of organometallic chemistry that has also enjoyed important development in recent years, due mainly to the use of polyhalophenyl groups, which confer the complexes a higher thermodynamic and kinetic stability. Thus, some reviews of arylgold chemistry have been published since 1986 [11–13], the last update coming in 1994 [14] with a more recent one (in 2005) dealing with arylgold(I) derivatives [15].

This review covers research on perfluoroarylgold chemistry since 1994. Earlier work is discussed only as background or for comparison purposes. It focuses not only on the different synthetic routes, but also on the crystal structures and the possible applications of the pentafluororphenyl derivatives described, such as those derived from the optical properties displayed by many gold – mainly monovalent – complexes and that have generated growing interest in the study and understanding of closed-shell metal–metal interactions. This has led to the synthesis of numerous examples of homo- or hetero-atomic associations displaying intra- or intermolecular metal–metal interactions and that can be obtained using several types of ligands. The complexes mentioned in this review are then organized according to the non-aryl ligand/s bonded to gold, ranging from the simplest (halides) to the non-classic ferrocene derivatives or metalloligands.

2. Group 17 donor atom ligands: halides

Arylhalide compounds are among the simplest perhalophenylgold derivatives and are usually obtained by displacement of the labile S-donor ligand tetrahydrothiophene (tht) form $[Au(C_6F_5)(tht)]$ in its reaction with an halide Eq. (1).

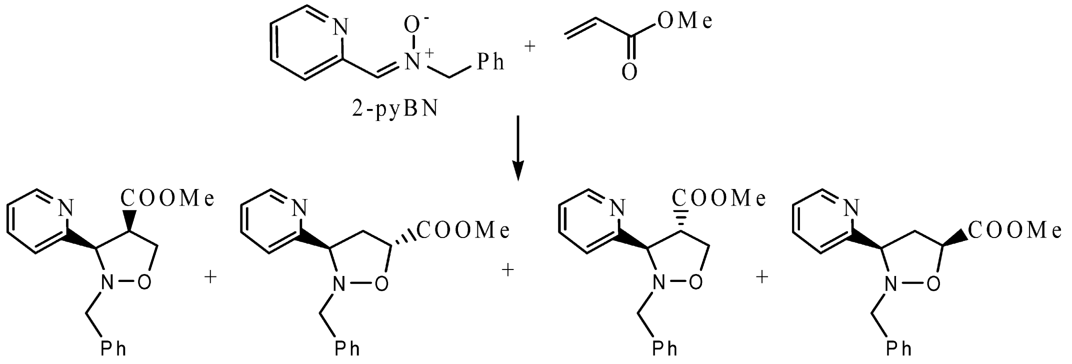
$$[Au(C_6F_5)(tht)] + QX \longrightarrow Q[Au(C_6F_5)X] + tht \qquad (1)$$

The anionic derivatives $PPN[Au(C_6F_5)Cl]$, $NMe_4[Au(C_6F_5)Cl]$ ($PPN = N(PPh_3)_2$) [16] or $(Me_3PC{\equiv}CPh)[Au(C_6F_5)Br]$ have recently been synthesized using this general method [17], although attempts to generate the phosphonium ylide complex $[Au(C_6F_5)\{CH_2{=}PMe_2(C{\equiv}CPh)\}]$ by treatment with a strong base were not successful. In contrast, the related phosphonium salt $(MePh_3P)[Au(C_6F_5)Br]$ leads to the corresponding ylide derivative $[Au(C_6F_5)(CH_2{=}PPh_3)]$ when treated with NaH, thus avoiding the need for prior preparation of the free ylide [18]. This last halide complex has been structurally characterized by X-ray diffraction methods, showing discrete linear molecules with Au–C and Au–Br distances of 2.009(5) and 2.4137(7) Å [19].

The crystal structure of the related complex $(BzPPh_3)[Au(C_6F_5)Cl]$ has also been previously determined, showing longer Au–C bond lengths (2.054(17) and 2.042(15) Å), which could be due to the greater *trans* influence of the bromine ligand [20]. Even greater is the *trans* influence of the pentafluorophenyl group, as deduced from the Au–C distances in the gold(III) anion $[Au(C_6F_5)_3Cl]^-$, whose crystal structure has been described with two different gold(I) cations: $[Au_3(\mu\text{-dppm})_2Cl_2]^+$ (dppm = bis(diphenylphosphino)methane) [21] and $[Au_4(\mu\text{-dpmp})_2Cl_2]^{2+}$ (dpmp = bis(diphenylphosphinomethyl)phenylphosphine) [22].

In an attempt to prepare new superconductor materials of gold the cation-radical salts $(TTF)[Au(C_6F_5)Cl]$, $(TTFPh_2)_{2.5}[Au(C_6F_5)_2Cl_2]$ or $(TTFPh_2)[Au(C_6F_5)_2I_2]$ (TTF = tetrathiafulvalene, $TTFPh_2$ = 4,4′-diphenyltetrathiafulvalene) have been synthesized by electrocrystallization, although they have only shown semiconductor behavior with an $E_a = 0.13$ eV in the range of 300–200 K [23]. This synthetic method consists in the treatment of the electron-donor molecule TTF or $TTFPh_2$ with the corresponding organoaurate salt containing a classical cation under a controlled current.

The electrochemistry of certain arylgold complexes has been studied by cyclic voltammetry, showing the reduction of Au(III) to Au(I) for Au(III) complexes and reduction of Au(I) to Au(0) for most of the Au(I) compounds [24]. Finally, a series of anionic and neutral pentafluorophenylgold(III) species have also been tested as a catalyst for the addition of water and methanol to terminal alkynes, concluding that they can efficiently mediate these reactions in neutral media in refluxing methanol [25]. The same species also mediate the 1,3-dipolar cycloaddition of *N*-benzyl-C(2-pyridil)nitrone (2-pyBN) and methylacrilate (Eq. (2)), decreasing reaction time and favoring the formation of the *exo* (*cis*) isomer [26].



(2)

In order to identify possible intermediates in the cycloaddition reaction, new nitrone derivatives [Au(C_6F_5)Cl_2(2-pyBN)] and [Au(C_6F_5)$_2$Cl(2-pyBN)] have been prepared by treating [Au(C_6F_5)Cl_2(tht)] or [Au(C_6F_5)$_2$(μ-Cl)]$_2$ with the free ligand [26].

3. Group 16 donor atom ligands

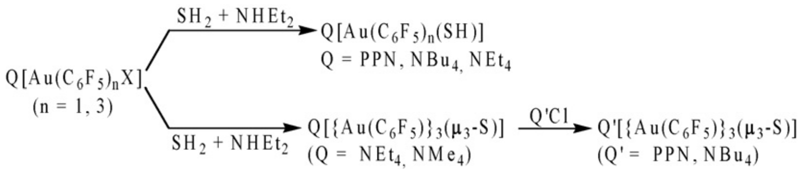
3.1. Sulfides and selenides

Treatment of halide complexes of the type Q[Au(C_6F_5)$_n$X] (n = 1, 3) with SH_2 in the presence of a base leads to the corresponding hydrosulfido derivatives Q[Au(C_6F_5)(SH)] (Q = PPN, NBu_4, NEt_4) or to trinuclear bridging sulfido complexes Q[{Au(C_6F_5)}$_3$(μ_3-S)] (Q = PPN, NBu_4, NEt_4, NMe_4) [16] (Scheme 1). The crystal structure of one of these trinuclear derivatives was determined by X-ray diffraction methods, showing the sulfur atom in a distorted trigonal pyramidal environment with Au···Au contacts between 3.1844(9) and 3.4772(9) Å and, correspondingly, a narrow Au–S–Au angle (86.68(12)–97.65(13)°). Two of these pairs of parameters are in the normal range observed for related sulfur-centered derivatives [27–30] (Au···Au 2.990(1)–3.420(1) Å; Au–S–Au 79.5(1)–95.0(3)°). All these Au···Au and Au–S–Au values are similar to those calculated for S$(AuPH_3)_3^+$ using relativistic potentials (Au···Au 3.05, 3.52 Å; Au–S–Au 82.3, 98.5°) [31].

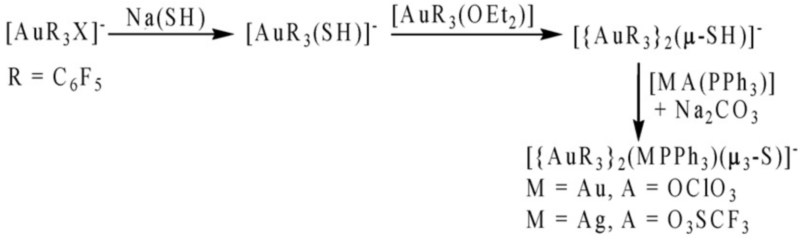
Similarly, the reaction of NBu_4[Au(C_6F_5)$_3$Br] with Na(SH) leads to the synthesis of NBu_4[Au(C_6F_5)$_3$(SH)], which then reacts with one equivalent of [Au(C_6F_5)$_3$(OEt_2)] to afford a dinuclear species with a bridging hydrosulfido ligand NBu_4[{Au(C_6F_5)$_3$}$_2$(μ-SH)] [32]. Its treatment with triphenylphsophinegold(I) or silver(I) starting materials and an excess of Na_2CO_3 leads to the trinuclear Au^{III}/M^{I} derivatives NBu_4[{Au(C_6F_5)$_3$}$_2$($MPPh_3$)(μ_3-S)] (M = Au, Ag) as shown in Scheme 2 [32]. The crystal structures of these last three complexes have been determined, showing a trigonal–pyramidal geometry at sulfur with no short Au–Au or Au–Ag interactions. The Au–C bond distances *trans* to sulfur are generally shorter than the *cis* ones, indicating a greater *trans* influence for the pentafluorophenyl group if compared to sulfide or hydrosulfide, and also greater than for PPh_3 as demonstrated by the Au–S bond lengths in NBu_4[{Au(C_6F_5)$_3$}$_2$($AuPPh_3$)(μ_3-S)], which are longer for gold(III) (2.374(5) Å) than for gold(I) (2.303(5) Å) in spite of the shorter radium of trivalent gold [32].

Other homo- or heteropolynuclear (from three- to heptanuclear) compounds containing a sulfide or selenide ligand bridging three or four gold atoms can be prepared by reaction of the phosphino derivatives [{Au(PPh_3)}$_2$(μ-E)] or [{Au_2(μ-dppf)}(μ-E)] (E = S, Se; dppf = 1,1′-bis(diphenylphosphino)ferrocene) with the appropriate pentafluorophenylgold(I) or gold(III) starting complexes as shown in Scheme 3 [33–36].

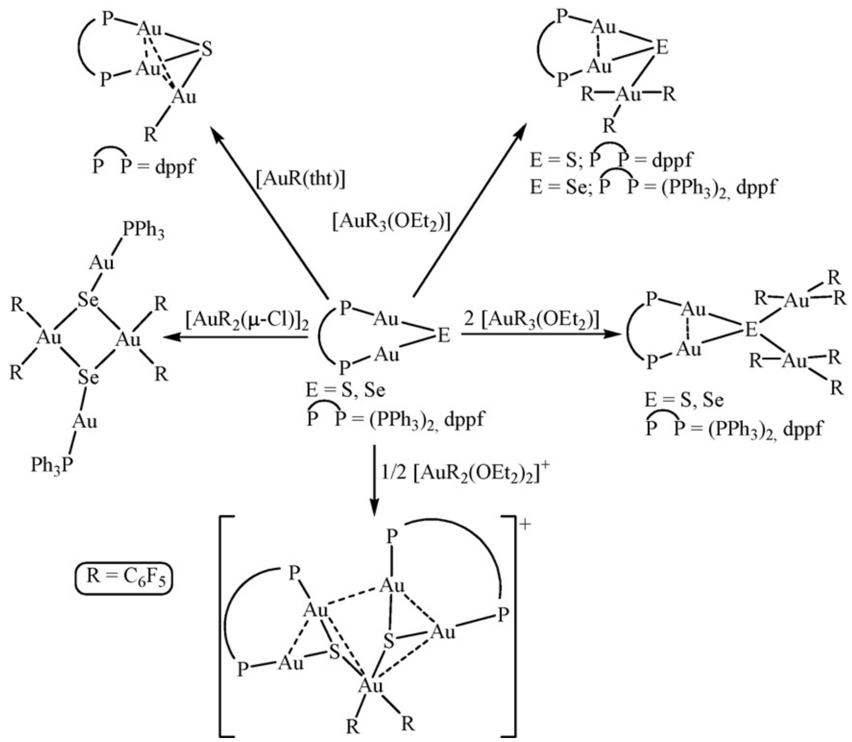
The crystal structures of some of these derivatives: [{Au(C_6F_5)$_3$}{Au_2(dppf)}(μ_3-E)] (E = S, Se) [35,36], [{Au(C_6F_5)$_3$}$_2${Au_2(dppf)}(μ_4-S)] [34], [{Au(C_6F_5)$_3$}$_2$-{Au(PPh_3)}$_2$(μ_4-S)] [34], [{μ-Au(C_6F_5)$_2$}{Au(PPh_3)}-(μ_3-Se)]$_2$ [36] and [{Au(C_6F_5)$_2$}{Au_2(dppf)(μ_3-S)}$_2$]OTf (OTf = trifluoromethylsulfonate, O_3SCF_3) [35] have been established by X-ray diffraction methods, with linear or square-planar gold(I) or gold(III) atoms, respectively. The geometry at the sulfur or selenium atoms is essentially trigonal pyramidal in the triply bridging sulfido or selenido complexes or tetrahedral in the μ_4-E derivatives. With the only exception of [{μ-Au(C_6F_5)$_2$}{Au(PPh_3)}(μ_3-Se)]$_2$, they show $Au^{I}\cdots Au^{I}$ aurophilic interactions in the range 2.8889(8)–3.2244(19) Å that are correlated with the narrower Au–E–Au angles (73.81(3)–87.75(11)°) and that compare well with those observed for related sulfur-centered derivatives [27–30,37,38]. There are also some $Au^{I}\cdots Au^{III}$ contacts, although these are always weaker than the $Au^{I}\cdots Au^{I}$ interactions. The Au–S distances are generally longer than in the starting materials and, as commented above, the Au(III)–S distances (ranging from 2.374(4) to 2.397(4) Å) are surprisingly longer than the Au(I)–S lengths (2.319(4)–2.368(4) Å). The same pattern is observed in the Au(III)–Se and Au(I)–Se bond distances, showing Au–Se lengths to gold(III) (2.4802(8)–2.5038(13) Å) longer than those to gold(I) (2.4225(9)–2.4569(11) Å). The Au^{I}–Se distances are



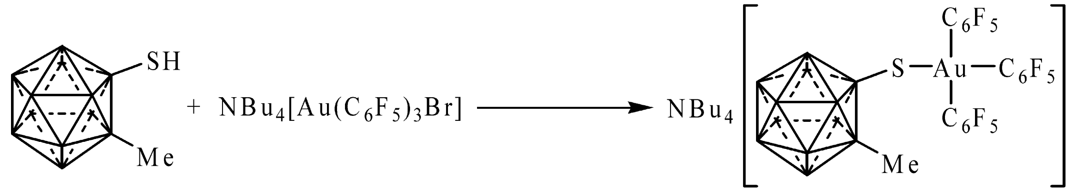
Scheme 1.



Scheme 2.

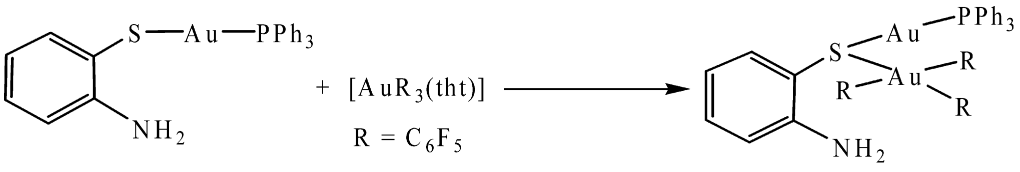


Scheme 3.



(3)

generally of the same order as those in the related complexes $[\{Au(PPh_3)\}_3(\mu_3\text{-}Se)]^+$ [39] or $[\{Au_2(dppf)\}\{Au_2(dppf)(\mu_4\text{-}Se)\}_2](OTf)_2$ [40] (2.4240(10)–2.4704(10) Å), while the Au^{III}–Se ones are longer than in $[AuCl_3(SePh_2)]$ (2.445(1) Å) [41].



(4)

3.2. Thiolates and selenolates

The potential use of thiolate gold(I) complexes in medicine, including uses as antiarthritic and cancerostatic drugs [42], has led to the synthesis of a great variety of thiols and their corresponding thiolate derivatives. One example of a non-classical thiol is the borane derivative 1-methyl-2-sulfanyl-1,2-dicarba-*closo*-dodecaborane ($HSCB_{10}H_{10}CMe$), which reacts with $NBu_4[Au(C_6F_5)_3Br]$ to afford the thiolate gold(III) derivative $NBu_4[Au(C_6F_5)_3(SCB_{10}H_{10}CMe)]$ [43] Eq. (3).

The dinuclear mixed gold(I)–gold(III) thiolate $[\{Au(C_6F_5)_3\}\{Au(PPh_3)\}(2\text{-}SC_6H_4NH_2)]$ is obtained by the reaction of $[Au(PPh_3)(2\text{-}SC_6H_4NH_2)]$ with one equivalent of $[Au(C_6F_5)_3(tht)]$, as shown in Eq. (4) [44].

Similarly, the homo- and heteropolynuclear thiolate or selenolate complexes $[\{Au(C_6F_5)_3(\mu\text{-}ER)\}_2\{Au_2(L,L)\}]$ (L,L = dppm, ER = 2-$SC_6H_4NH_2$; L,L = dppf, ER = SC_6F_5, SePh), $[\{\mu\text{-}Au(C_6F_5)_3\}(\mu\text{-}SePh_2)_2\{Au_2(dppf)\}]$ or $[\{Au(C_6F_5)_2\}\{(\mu_3\text{-}SC_6F_5)(Au_2dppf)\}_2](ClO_4)_3$ [44–46] can be prepared when thiolate- or selenolatephosphinogold(I) complexes of the type $[\{Au_2(\mu\text{-}L,L)\}(ER)]$ (L,L = dppm, ER = 2-$SC_6H_4NH_2$; L,L = dppf, ER = SC_6F_5, SePh) are treated with gold(III) reagents containing labile ligands.

Some of them have been characterized by X-ray diffraction methods. Complex $[\{Au(C_6F_5)_3(\mu\text{-}2\text{-}SC_6H_4NH_2)\}_2\{Au_2(dppm)\}]$ [44], which crystallizes with two independent molecules in the asymmetric unit, shows both Au^I–Au^I and Au^I–Au^{III} contacts of different magnitude

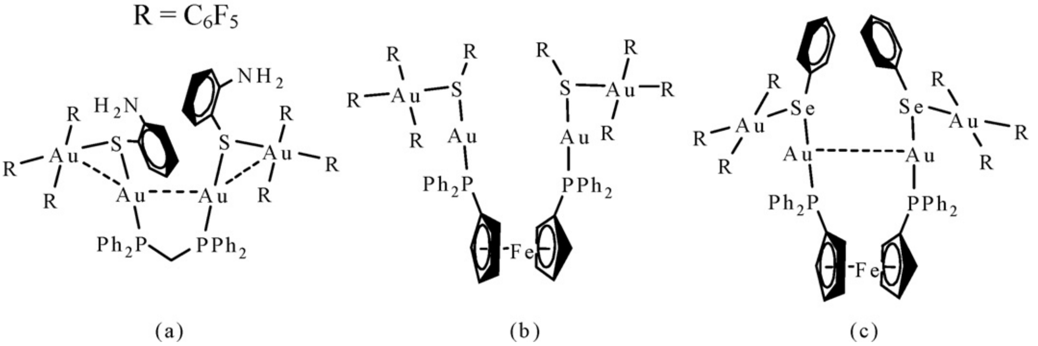


Fig. 1. $R = C_6F_5$.

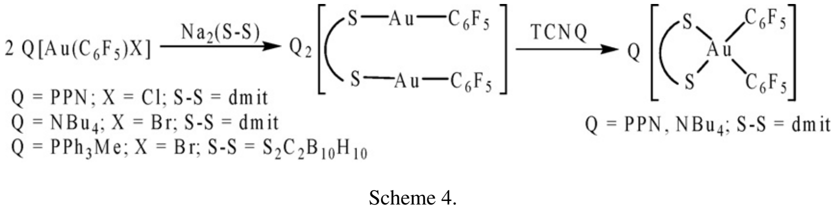
(Fig. 1a). After complexation of the gold(III) fragments, there is a shortening of the $Au^I–Au^I$ distance to 2.9353(7) and 2.9332(7) Å [3.1346(4) Å in the starting compound]. The $Au^I–Au^{III}$ lengths range from 3.2812(7) to 3.4052(7) Å, shorter than in other sulfide, thiolate, or selenide-mixed derivatives [3.404(1)–4.011(1) Å] [34–36]. In the crystal structure of the heteropentanuclear $[\{Au(C_6F_5)_3(\mu\text{-}SC_6F_5)\}_2\{Au_2(dppf)\}]$ [45], the $Au^I–Au^I$ distance of 3.834(2) Å is too long to be considered a significant interaction, and is longer than the $Au^I–Au^{III}$ distance (3.608(2) Å) (Fig. 1b). Lastly, in $[\{Au(C_6F_5)_3(\mu\text{-}SePh)\}_2\{Au_2(dppf)\}]$ [46] an intermediate situation has been observed, with $Au^I–Au^I$ distances shorter than the $Au^I–Au^{III}$ lengths (3.693 and 3.578 Å) (Fig. 1c). As expected, all of them show linear and square-planar gold(I) and gold(III) atoms, respectively, and, as in the structures commented above, the Au(III)–S (2.372(3)–2.380(2) Å) or Au(III)–Se distances (2.4878(4) and 2.4896(4) Å) are again longer than the Au(I)–S (2.332(3)–2.342(3) Å) or Au(I)–Se lengths (2.4408(5)–2.4392(5) Å), and the Au(III)–C distances confirm the greater *trans* influence of the perhalophenyl group when compared with the thiolate or selenolate.

When dithiolate ligands are used instead of thiolate ones, anionic dinuclear gold(I) species containing the sulfur donor ligands 2-thioxo-1,3-dithiole-4,5-dithiolate ($C_3S_5{}^{2-}$, dmit) [47] or 1,2-dithiolate-*o*-carborane [48] can be prepared by reaction of pentafluorophenylhaloaurate(I) with the ligand (deprotonated in situ) in a 2:1 molar ratio, as shown in Scheme 4. In these complexes, the dithiolate acts as a bridging ligand between two gold(I) complexes, but it can be transformed into a chelate ligand by oxidation of $Q[\{Au(C_6F_5)\}_2(dmit)]$ ($Q = PPN$, NBu_4) with 7,7,8,8-tetracyanoquinodimethane (TCNQ), affording the gold(III) derivatives $Q[Au(C_6F_5)_2(dmit)]$ [47]. A similar complex in which the bidentate sulfur donor ligand acts as chelate is the carborane derivative $NBu_4[Au(C_6F_5)_2(S_2C_2B_{10}H_{10})]$, obtained from $NBu_4[Au(C_6F_5)_2Cl_2]$ and $H_2S_2C_2B_{10}H_{10}$ under basic conditions [49].

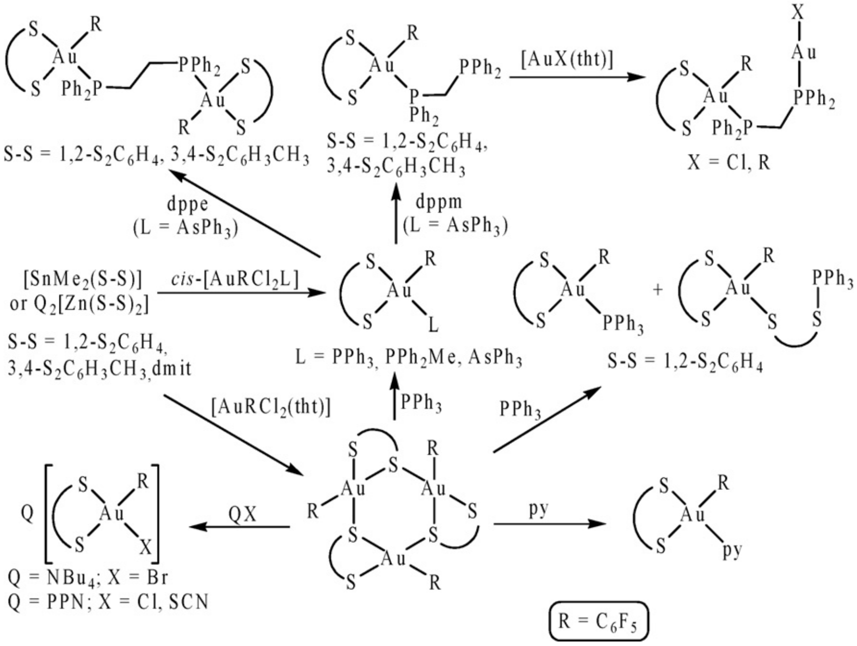
A number of neutral dithiolate gold(III) complexes with general formula $[Au(C_6F_5)(S–S)L]$ and with the bidentate ligand acting as chelate can be prepared by reaction of *cis*-$[Au(C_6F_5)Cl_2L]$ with tin or zinc reagents of the types $[SnMe_2(S–S)]$ or $Q_2[Zn(S–S)_2]$, which can transfer the dithiolate group under mild conditions [50] (see Scheme 5). The labile ligand triphenylarsine can be easily displaced from $[Au(C_6F_5)(S–S)(AsPh_3)]$ [S–S = 1,2-benzenedithiolate ($1,2\text{-}S_2C_6H_4{}^{2-}$), 3,4-toluenedithiolate ($3,4\text{-}S_2C_6H_3CH_3{}^{2-}$)] by treatment with diphosphines to yield $[Au(C_6F_5)(S–S)(dppm)]$ or $[\{Au(C_6F_5)(S–S)\}_2(dppe)]$ (dppe = bis(diphenylphosphino)ethane) [51]. The dppm derivatives, which display a free phosphorus atom, can also react with an equimolecular amount of $[AuX(tht)]$ ($X = Cl$, C_6F_5) to produce Au^I/Au^{III} products $[Au(C_6F_5)(S–S)(dppm)AuX]$ [51].

If *cis*- or *trans*-$[Au(C_6F_5)Cl_2(tht)]$ is used instead of *cis*-$[Au(C_6F_5)Cl_2L]$ in the reaction with $[SnMe_2(S–S)]$ or $Q_2[Zn(S–S)_2]$ in acetone or dichloromethane, a different result is obtained as a consequence of the displacement of tht, and thus the trinuclear cyclic compounds $[Au(C_6F_5)(S–S)]_3$ (S–S = $1,2\text{-}S_2C_6H_4$, $3,4\text{-}S_2C_6H_3CH_3$, dmit) are isolated and from the mother liquors $[SnMe_2Cl_2]$ or $Q_2[ZnCl_4]$ are recovered [52]. These trimers react under very mild conditions with neutral or anionic ligands or give dithiolates of formula $[Au(C_6F_5)(S–S)L]$ [L = PPh_3, py (pyridine)] or $Q[Au(C_6F_5)(S–S)X]$, respectively [52], as shown in Scheme 5. When S–S = $1,2\text{-}S_2C_6H_4$ is used, a small quantity of pink complex precipitates, identified as $[Au(C_6F_5)(1,2\text{-}S_2C_6H_4)(SC_6H_4SPPh_3)]$ and containing a new thiolate ligand formed by an unprecedented coupling of triphenylphosphine and one S terminus of dithiolate [52].

The molecular structures of the complexes $PPN[Au(C_6F_5)_2(dmit)]$ [47], $[Au(C_6F_5)(1,2\text{-}S_2C_6H_4)(PPh_3)]$ [50], $[Au(C_6F_5)(1,2\text{-}S_2C_6H_4)(SC_6H_4SPPh_3)]$ [52] and $[Au(C_6F_5)(1,2\text{-}S_2C_6H_4)(dppm)Au(C_6F_5)]$ [51] have been established by X-ray diffraction studies. All of them exhibit square-planar geometry at gold(III), contain chelate dithiolate



Scheme 4.



Scheme 5.

ligands and the 1,2-benzenedithiolate derivatives display very similar [Au(C_6F_5)(1,2-$S_2C_6H_4$)] fragments. The Au–C distances, which range from 2.059(5) to 2.07(2) Å, compare well with those in other pentafluorophenylgold(III) complexes [Au(C_6F_5)$_4$]$^-$ (2.054(7)–2.058(8) Å) [53,54] and [Au(C_6F_5)$_2${$S_2CN(CH_2Ph)_2$}] (2.047(6)–2.049(6) Å) [55]. The comparison of the Au–S distances *trans* to C_6F_5 (2.308(3)–2.324(2) Å) with the Au–S distance *trans* to PPh_3 (2.299(1) Å) or to dppm (2.296(3) Å) reflects a higher *trans* influence of the pentafluorophenyl group compared to phosphines [56]. These distances are very similar to those observed in the bis(dithiolate) complexes [Au{$S_2C_2(CN)_2$}$_2$]$^-$ (2.309 Å) [57], [Au(1,2-$S_2C_6H_4$)$_2$]$^-$ (2.305 Å) [58] or [Au(3,4-$S_2C_6H_3CH_3$)$_2$]$^-$ (2.287(3) and 2.329(4) Å) [59]. Finally, the Au–P distances of 2.340(1) and 2.336(3) Å compare well with those for [$AuCl_3(PPh_3)$] (2.335(4) Å) [60] or [$AuMe_3(PPh_3)$] (2.350(6) and 2.347(6) Å) [61]. In the dinuclear complex the Au^{III}–C and Au^{III}–P lengths (2.060(11) and 2.336(3) Å, respectively) are longer than the Au^{I}–C and Au^{I}–P lengths of 2.039(12) and 2.264(3) Å, respectively, following the same unexpected tendency that the Au–S bond distances in the thiolate derivatives described above.

Finally, the molecular structure of the trinuclear product [Au(C_6F_5)(1,2-$S_2C_6H_4$)]$_3$ [52], which displays crystallographic threefold symmetry, shows the central six-membered Au_3S_3 ring in a chair configuration (Fig. 2) and a slightly distorted square-planar arrangement for the gold centers. One sulfur atom of each benzenedithiolate ligand bridges a pair of gold atoms and is thus three-coordinate, while the other only binds one gold atom. The relatively short Au–Au distance of 3.515 Å is very similar to the 3.563 and 3.545 Å in [Au(CH_3)$_2$$NH_2$]$_3$ [62] and is probably imposed by the ring. The Au–S distances differ significantly and those to the bridging S are, as expected, longer (2.352(2) and 2.395(2) Å) than the other one (2.292(2) Å), although surprisingly the Au–S *trans* to S is longer than the Au–S *trans* to C in spite of the appreciable *trans* influence of carbon ligands at gold.

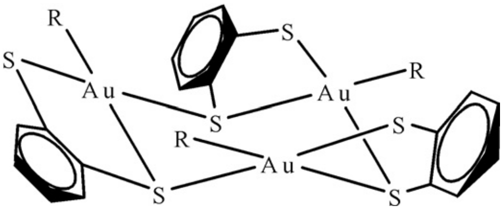
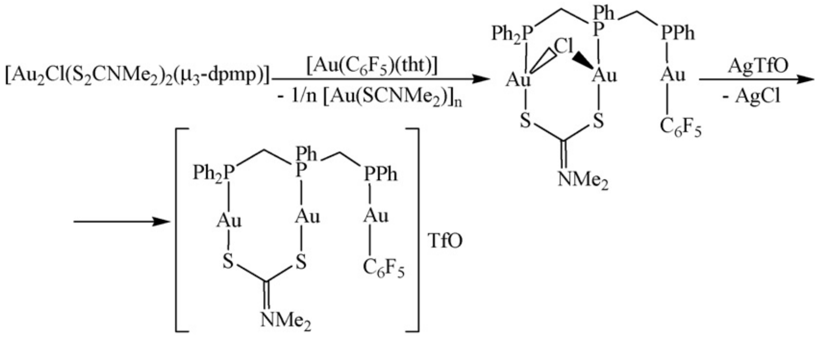


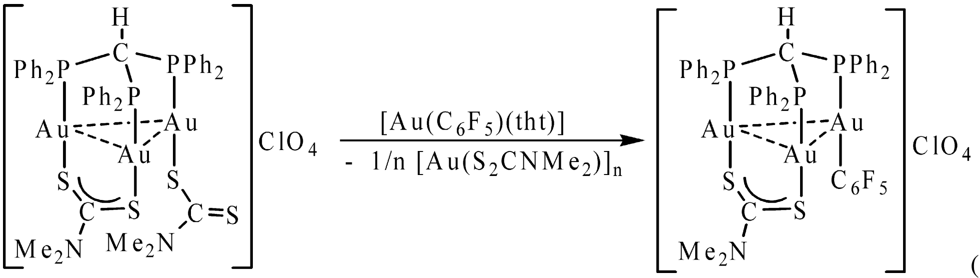
Fig. 2. R = C_6F_5.

3.3. Dithiocarbamates

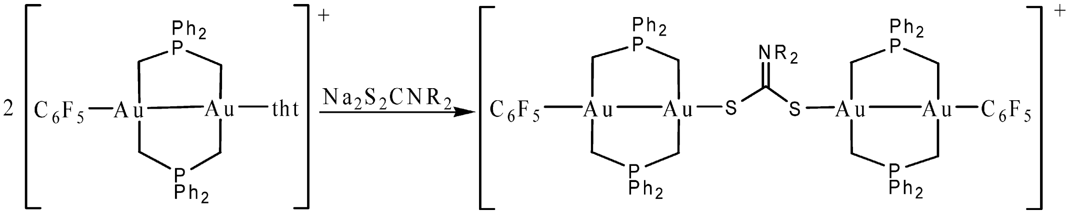
Dithiocarbamate and their derivatives have also been frequently employed as S-donor ligands for the synthesis of gold compounds due to their applications as vulcanization accelerators, flotation agents, fungicides and pesticides, and their antimicrobial activity has also been reported [63–65]. They usually act as bidentate ligands bridging two metal atoms, although a few gold complexes containing monodentate dithiocarbamates have also been reported, such as [Au_3(μ-S_2CNMe_2)$_2${μ$_3$-(PPh_2)$_3$CH}]ClO_4 [66]. In order to test the coordinative ability of the free sulfur atom that this species presents, it was treated with [Au(C_6F_5)(tht)]. However, this reaction, instead of promoting coordination of the new metallic center to the sulfur, resulted in the precipitation of gold(I) dimethyldithiocarbamate and the coordination of the pentafluorophenyl group to the gold center previously bonded to $S_2CNMe_2$$^-$, as shown in Eq. (5) [66].



Scheme 6.



(5)



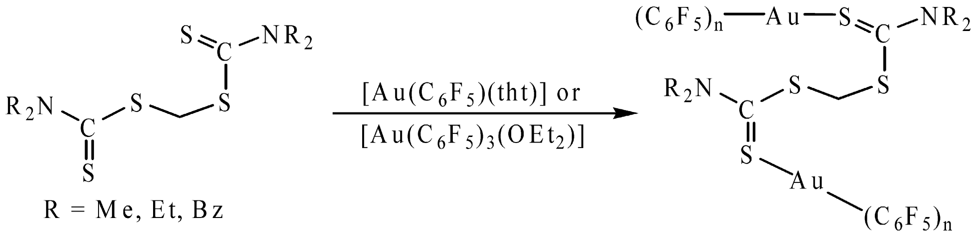
(6)

In a similar reaction, the insolubility of the polymeric species $[Au(S_2CNMe_2)]_n$ also enabled the synthesis of the neutral $[Au_3(C_6F_5)Cl(\mu\text{-}S_2CNMe_2)(\mu_3\text{-dpmp})]$ (see Scheme 6). This arrangement of ligands, with dithiocarbamate and chloride acting as bridges, is proposed on the basis of its $^{31}P\{^1H\}$ NMR spectrum, which implies that this complex should be a racemic mixture. This complex can also be transformed into the cationic derivative $[Au_3(C_6F_5)(\mu\text{-}S_2CNMe_2)(\mu_3\text{-dpmp})]TfO$ (TfO = trifluoromethylsulfonate, SO_3CF_3) by elimination of the chlorine atom as silver chloride when it reacts with AgTfO [67].

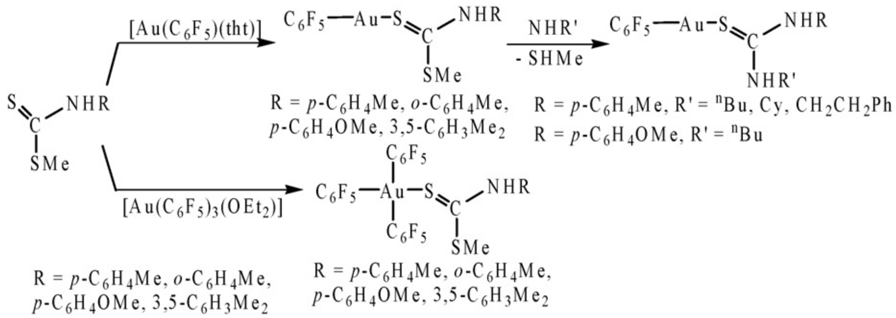
In the tetranuclear gold(II) products $[\{Au_2(C_6F_5)(\mu\text{-}CH_2PPh_2CH_2)_2\}_2(\mu\text{-}S_2CNR_2)]ClO_4$ (R = Me, Et, Bz), obtained by displacement of tht from $[Au_2(C_6F_5)(\mu\text{-}CH_2PPh_2CH_2)_2(tht)]ClO_4$ when treated with $Na_2S_2CNR_2$ (2:1) (Eq. (6)), dialkyldithiocarbamate also acts as bidentate and bridges two dinuclear bis(ylide) units [68].

The presence of a methyl group bonded to one of the sulfur atoms of the dithiocarbamate favors monodentate coordination. Thus, reaction of methyl dithiocarbamates S(MeS)CNHR (R = *p*-C_6H_4Me, *o*-C_6H_4Me, *p*-C_6H_4OMe, 3,5-$C_6H_3Me_2$) with $[Au(C_6F_5)(tht)]$ or $[Au(C_6F_5)_3(OEt_2)]$ gives the corresponding mononuclear gold(I) or gold(III) derivatives $[Au(C_6F_5)_n\{S(MeS)CNHR\}]$ ($n = 1, 3$) containing S-donor ligands [69]. Reaction of the gold(I) complexes with primary amines results in the thioacylation of the primary amines affording the neutral complexes $[Au(C_6F_5)_n\{S(R'HN)CNHR\}]$ (R = *p*-C_6H_4Me, R′ = ^{n}Bu, Cy, CH_2CH_2Ph; R = *p*-C_6H_4OMe, R′ = ^{n}Bu) in low yields and mercaptanes [69] (see Scheme 7).

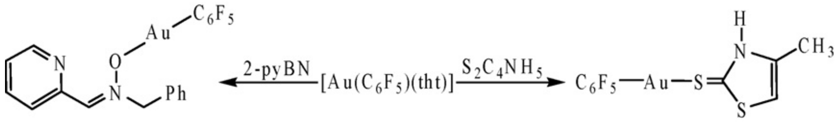
Finally, when the methylenebis(dialkyldithiocarbamates) $CH_2(S_2CNR_2)_2$ (R = Me, Et, Bz) is used in the reaction with the same gold(I) or gold(III) precursors as above, the dinuclear species $[\{Au(C_6F_5)_n\}_2\{CH_2(S_2CNR_2)_2\}]$ ($n = 1$, 3), coordinated to gold *via* the C=S function, are isolated [70] (Eq. (7)).



(7)



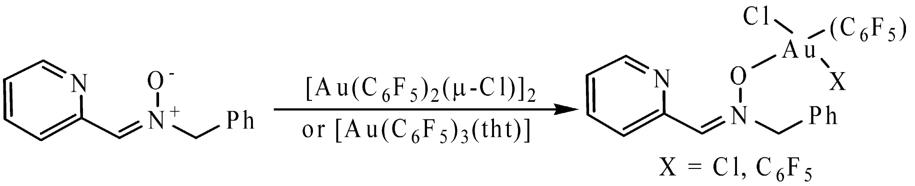
Scheme 7.



Scheme 8.

3.4. Small neutral molecules with group 6 donor atoms

As commented in Section 2, the gold(III) nitrone derivatives [Au(C_6F_5)Cl_2(2-pyBN)] (2-pyBN = *N*-benzyl-C(2-pyridil)nitrone) and [Au$(C_6F_5)_2$Cl(2-pyBN)], which are possible intermediates in the cycloaddition of 2-pyBN and methylacrilate, have been obtained according to Eq. (8) [26].



(8)

Similarly, treatment of equimolecular amounts of [Au(C_6F_5)(tht)] with the same nitrone or the thiazole–thione ligand $S_2C_4NH_5$ readily affects the substitution of the tht to produce the gold(I) complexes [Au$(C_6F_5)_2$Cl(2-pyBN)] or [Au(C_6F_5){S=CN(H)C(CH_3)=C(H)S}], respectively (Scheme 8) [26,71].

The latter has been characterized by X-ray diffraction methods, showing a linear environment for the gold(I) atom by coordination to almost coplanar perfluorophenyl and thione ligands with Au–C and Au–S bond lengths of 2.057(14) and 2.304(4) Å, respectively [71]. Although gold(I) complexes of the type [AuRL] frequently associate into pairs *via* Au–Au contacts, no aurophilic interactions were observed in this case, although hydrogen bonding and arene–arene interactions seem to dominate lattice organization. As a result of the N–H···F interactions of 3.203(15) and 3.320(17) Å, the molecules in the crystal were arranged in sheets, in which the molecules were arranged to form dimers with the molecules in the neighboring sheets *via* Au···S contacts (see Fig. 3) with Au–S distances of 3.529(4) Å. This general pattern was also observed in [Au(SCN)(2,6-$NC_6H_3Me_2$)] (Au–S 3.459(2) Å) and [Au(SCN)(2,3,6-$NC_6H_2Me_3$)] (Au–S 3.938(2) and 3.719(2) Å) [72].

Tetrahydrothiophene complexes [Au$(C_6F_5)_n$(tht)] (n = 1, 3) have been known for a long time [73,74] and have been used extensively as starting materials in the coordination chemistry of gold, but surprisingly their crystal structure determinations have only been reported very recently [75] together with the synthesis and crystal structure of another two pentafluorophenyl gold products with tht as ligand. A unique rearrangement of [Au$(C_6F_5)_3$(tht)] in solution affects ionic compound formation between two gold(III) complexes in [Au$(C_6F_5)_2$$(tht)_2$][Au$(C_6F_5)_4$], and by reaction of [Au(C_6F_5)(tht)] and [Au$(C_6F_5)_3$(tht)] the gold(II) compound [$Au_2$$(C_6F_5)_4$$(tht)_2$] is obtained as a crystalline product, representing the first example of an unbridged complex with a formal $[Au_2]^{4+}$ core in which the gold centers are not stabilized by any chelating ligand.

The crystal structure of [Au(C_6F_5)(tht)] shows linear monomers with paddle-like geometries forming an infinite chain

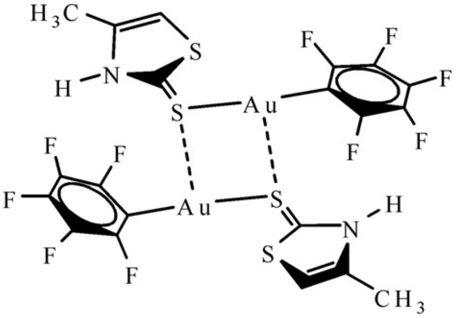


Fig. 3. Dimers of [Au(C_6F_5){S=CN(H)C(CH_3)=C(H)S}]

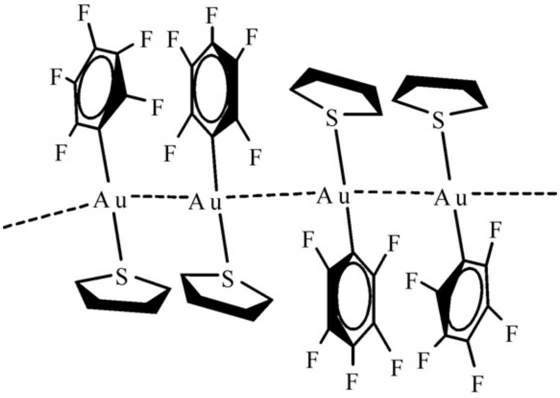


Fig. 4. Chains of $[Au(C_6F_5)(tht)]$

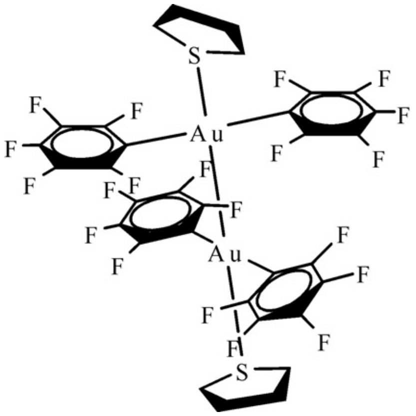


Fig. 5. Structure of $[Au_2(C_6F_5)_4(tht)_2]$

along the a axis through alternating long (3.306 Å) and short (3.191 and 3.128 Å) aurophilic interactions. Alternating pairs of molecules are rotated 180° (Fig. 4). The Au–C (2.014(9) and 2.03(1) Å) and Au–S (2.317(3) and 2.320(3) Å) bond distances compare well with those observed in the nitrone derivative commented above.

Crystals of the gold(III) compound $[Au(C_6F_5)_3(tht)]$ were obtained in two polymorphic forms, with the orientation of the tht as the only obvious difference between the two polymorphs. Owing to the large mutual *trans* influence of the two opposing C_6F_5 ligands, their Au–C lengths (2.067(3) Å) are longer than when the pentafluorophenyl ligand is *trans* to tht (2.031(3) Å). The Au–C and Au–S (2.3754(9) Å) bond lengths are in close agreement with those observed in $[Au(C_6F_5)_3(S_2PEt_3)]$ (2.067(4), 2.076(4) and 2.037(3), and 2.366(1) Å, respectively) [76].

In the ionic compound $[Au(C_6F_5)_2(tht)_2][Au(C_6F_5)_4]$, the homoleptic anion has the same propeller-like appearance as reported for $PPN[Au(C_6F_5)_4]$ [53] with Au–C bond lengths in the range 2.050(6)–2.065(6) Å. The cation contains a gold(III) center comparable to that in the complex $[Au(C_6F_5)_2(tht)_2]TfO$ [77] displaying mutual pentafluorophenyl ligands with Au–C distances of 2.066(7) Å.

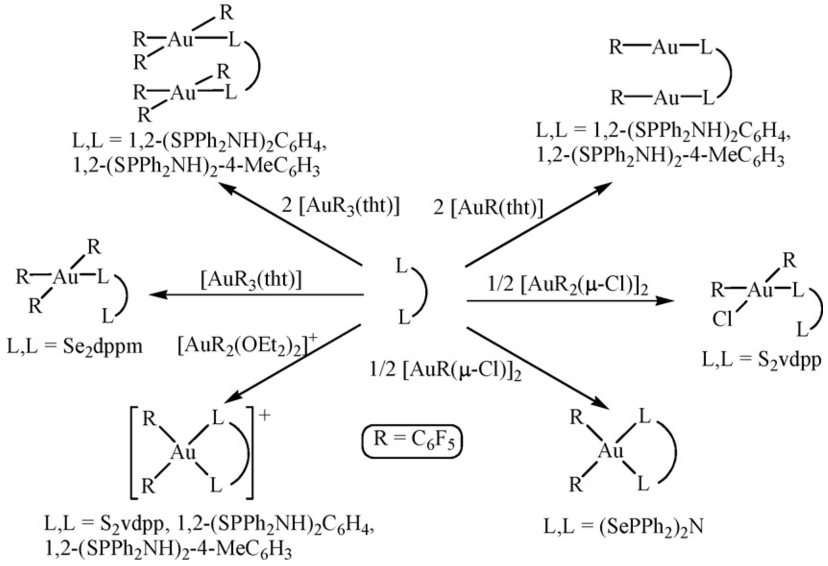
Finally, in the gold(II) derivative $[Au_2(C_6F_5)_4(tht)_2]$ the gold atoms occur in two distorted square-planar configurations, featuring an essentially linear S–Au–Au–S axis and two orthogonally oriented C_6F_5–Au–C_6F_5 moieties with all aromatic rings in parallel planes (see Fig. 5). The Au(II)–Au(II) bond length of 2.567(7) Å is within the range of interactions displayed by the unbridged Au^{II}–Au^{II} compounds (2.5355(5)–2.6405(8) Å) [78–80]. The Au–C (2.110(2) and 2.078(2) Å) and Au–S (2.418(3) Å) bond lengths are longer than in the rest of the pentafluorophenyl tetrahydrothiophene complexes, with decreasing lengths in the order $Au^{II} > Au^{III} > Au^{I}$.

3.5. Phosphine or methanide sulfides and selenides

Most common neutral ligands with sulfur or selenium as donor atoms are phosphine sulfides or selenides, which readily displace tht or diethyl ether from gold(I) or gold(III) starting materials such as $[Au(C_6F_5)_n(tht)]$ ($n = 1$, 3) or $[Au(C_6F_5)_2(OEt_2)_2]ClO_4$ to afford mono- or dinuclear complexes of the types $[Au(C_6F_5)_3(L,L)]$ [81], $[Au(C_6F_5)_2(L,L)]ClO_4$ [82,83] or $[\{Au(C_6F_5)_n\}_2(L,L)]$ [82] ($n = 1$, 3; L,L = diphosphine disulfide or diselenide) according to the procedure shown in Scheme 9. Similarly, reaction of S_2vdpp [S_2vdpp = vinylidenebis(diphenylphosphine) disulfide, $(SPPh_2)_2C=CH_2$] with $[Au(C_6F_5)_2(\mu\text{-}Cl)]_2$ in a 2:1 molar ratio leads to the rupture of the chlorine bridges to give the monodentate $[Au(C_6F_5)_2Cl\{SPPh_2C(=CH_2)PPh_2S\}]$ [83]. When the same reactions are performed using potassium diselenoimidodiphosphinato ($K[(SePPh_2)_2N]$) instead of S_2vdpp, the precipitation of potassium chloride forces the coordination of the ligand as a chelating ligand, leading to the synthesis of the neutral compound $[Au(C_6F_5)_2\{(SePPh_2)_2N\}]$ [84].

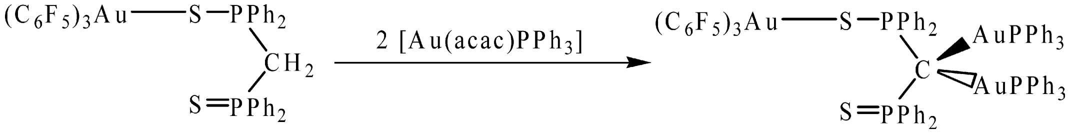
X-ray diffraction studies have been performed for two of these derivatives, $[\{Au(C_6F_5)_3\}_2(1,2\text{-}(SPPh_2NH)_2\text{-}4\text{-}MeC_6H_3)]$ [82] and $[Au(C_6F_5)_2\{(SePPh_2)_2N\}]$ [84], showing the typical square-planar environment for the gold(III) centers. The crystal structure of the former is similar to that of the related complex $[\{Au(C_6F_5)_3\}_2(1,2\text{-}(PPh_2NH)_2\text{-}4\text{-}MeC_6H_3)]$ [82], although the backbone conformation is much more regular with approximate twofold symmetry, and neither of these two compounds display aurophilic interactions (Au···Au separations of 7.631(3) and 8.972(2) Å, respectively). The Au–C distances for the mononuclear derivative (2.052(2) and 2.055(2) Å) lie in the range of Au–C bond lengths found for the dinuclear derivative (2.039(19)–2.08(2) Å), displaying similar distances for the Au–C bonds *trans* to sulfur or selenium, and they also compared well with the Au^{III}–C distances *trans* to sulfur observed in the complexes commented above. The Au–S distances in $[\{Au(C_6F_5)_3\}_2(1,2\text{-}(SPPh_2NH)_2\text{-}4\text{-}MeC_6H_3)]$ [82] (2.403(5) and 2.400(5) Å) are longer than the Au–S distances *trans* to C_6F_5 in the complexes described in previous sections (2.308(3)–2.324(2) Å) [47,50–52,72], while the Au–Se lengths in $[Au(C_6F_5)_2\{(SePPh_2)_2N\}]$ [84] (2.4808(3) and 2.4832(3) Å) are close to the Au(III)–Se distances found in the selenium derivatives commented above (2.4802(8)–2.5038(13) Å) [34–36,46].

The diphosphine disulfide complexes $[Au(C_6F_5)_3(SPPh_2CH_2Ph_2P=S)]$ or $[Au(C_6F_5)_2\{(SPPh_2)_2CH_2\}]ClO_4$ afford the methanediide derivatives $[Au(C_6F_5)_3\{SPPh_2C(AuPPh_3)_2$

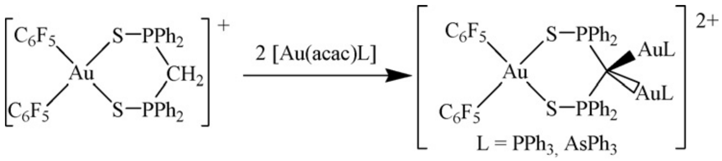


Scheme 9.

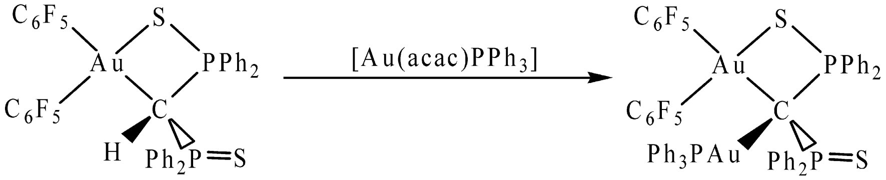
$Ph_2P=S\}]$ or $[Au(C_6F_5)_2\{(SPPh_2)_2C(AuL)_2\}]ClO_4$ (L = PPh_3, $AsPh_3$) in a one-step reaction when treated with two equivalents of [Au(acac)L] (acac = acetylacetonate) with the simultaneous formation of acetylacetone that remains in the mother liquors (Eqs. (9) and (10)) [85]. Similarly, when the starting complex is the S, C-donor $[Au(C_6F_5)_2(SPPh_2CHPh_2P=S)]$, reaction with $[Au(acac)(PPh_3)]$ (1:1) leads to the synthesis of $[Au(C_6F_5)_2\{SPPh_2C(AuPPh_3)Ph_2P=S\}]$ as shown in Eq. (11) [85]. The crystal structure of the triphenylarsine compound has been established by X-ray diffraction methods, showing the methanediide ligand acting as an eight electron-donor bridging three metal atoms and the gold(I) centers in this complex appear only 2.873(2) Å from each other [85].



(9)



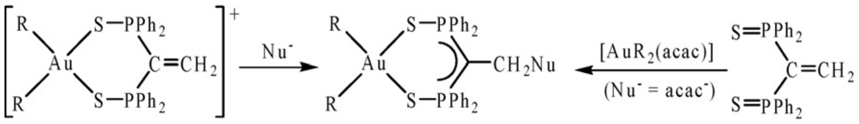
(10)



(11)

$[Au(C_6F_5)_2\{(SPPh_2)_2C=CH_2\}]ClO_4$ reacts rapidly with carbon- or oxygen-donor nucleophiles (Nu^-) to form the methanide-type derivatives $[Au(C_6F_5)_2\{(SPPh_2)_2CCH_2Nu\}]$ [Nu = acac, CN, C_5H_5, OEt] [83], products that can be considered as intermediates in Michael-type additions of HNu to the C=C bond, which are particularly stable in this case. The acetylacetonate derivative can also be prepared by treatment of the free ligand S2vdpp with $[Au(C_6F_5)_2(acac)]$, which contains the nucleophile in the gold starting material [83] (see Scheme 10).

The crystal structure of the cyclopentadienyl derivative [83] (Fig. 6) resembles that of $[Au(C_6F_5)_2\{(SePPh_2)_2N\}]$, with a square-planar geometry for gold and Au–C (2.033(3) and 2.032(3) Å) and Au–S lengths (2.3552(9) and 2.3626(9) Å) shorter than in $[Au(C_6F_5)_2\{(SePPh_2)_2N\}]$ (2.052(2) and 2.055(2) Å) [84] or $[\{Au(C_6F_5)_3\}_2(1,2\text{-}(SPPh_2NH)_2\text{-}4\text{-}MeC_6H_3)]$ (2.403(5) and 2.400(5) Å) [82], respectively. The P–C bond lengths to the methanide carbon are 1.709(3) and 1.719(3) Å, shorter than those found in complexes with the diphosphine, such as $[AuCl\{PPh_2C(C=CH_2)PPh_2\}]_2$ (1.828(6) and 1.833(6) Å) [86]. This, together with the C–C distance of 1.538(4) Å, indicates that the negative charge of the methanide carbon is delocalized over the P–C bonds, conferring them a degree of multiple



Scheme 10. R = C_6F_5. Nu^- = $acac^-$, CN^-, $C_5H_5{}^-$, $OEt_2{}^-$.

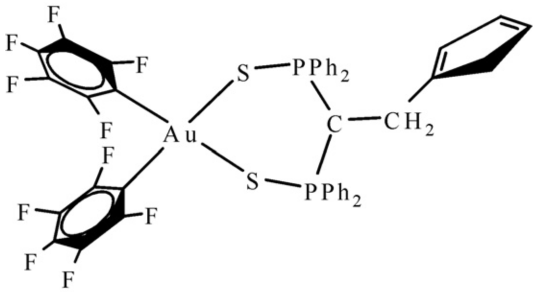


Fig. 6. Structure of $[Au(C_6F_5)_2\{SPPh_2)_2CCH_2(C_5H_5)\}]$

bonding.

When the same gold reagent as before reacts with Se_2dppm, which contains extractable hydrogen atoms, the reaction occurs with deprotonation of the methylene group, and the methanide complex $[Au(C_6F_5)_2(SePPh_2CHPPh_2Se)]$ is obtained [81], with a bidentate chelate Se, C coordination to the gold(III) center. The free selenium atom also reacts with $[Au(C_6F_5)_3(tht)]$ to give the dinuclear species $[Au(C_6F_5)_2\{SePPh_2CHPPh_2SeAu(C_6F_5)_3\}]$ [81] (Scheme 11).

In the molecular structure of the latter, the two gold(III) centers are coordinated to the ligand in a different manner: bidentate chelate and monodentate [81]. The Au–Se lengths of 2.4639(4) and 2.4940(4) Å are significantly different, more so than those found in $[Au(C_6F_5)_2\{(SePPh_2)_2N\}]$ [84] (2.4808(3) and 2.4832(3) Å). The Au–C bond distances to pentafluorophenyl lie in the range 2.048(3)–2.077(3) Å and seem to indicate a higher *trans* influence for the C_6F_5 groups than for the Se-donor ligand. The longest Au–C distance is that to the methanide carbon atom (2.153(3) Å), and is similar to those observed in methanide complexes, such as $[Au(C_6F_5)_3\{SPPh_2CH(AuC_6F_5)PPh_2CHCOOMe\}]$ (2.119(21) Å) [87].

4. Group 15 donor atom ligands

4.1. N-donor ligands

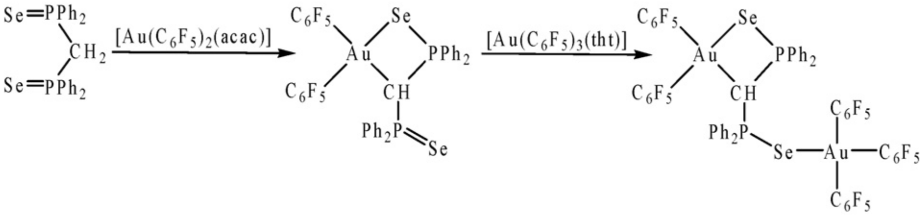
A number of mononuclear complexes of the type $[Au(C_6F_5)L]$ (L = 4-methylthiazole, its thioether $CH_3S\overline{C{=}NC(CH_3){=}C(H)S}$, piperidine [71], benzophenoneimine [88], 3-picoline [89], diphenyldiazomethane [90] or 2-aminothiazoline (2-amino-4,5-dihydrothiazole or 2-amt) [91]) have recently been prepared by rapid displacement of the weakly coordinated tetrahydrothiophene ligand from the precursor with different types of nitrogen donor ligands (Eq. (12)). Nitrogen coordination in the two first imine complexes has been confirmed by ^{15}N NMR [71] and the crystal structures of four of them have been determined exhibiting the expected linear N-coordination [71,88–90].

$$[Au(C_6F_5)(tht)] + L \longrightarrow [Au(C_6F_5)L] + tht \tag{12}$$

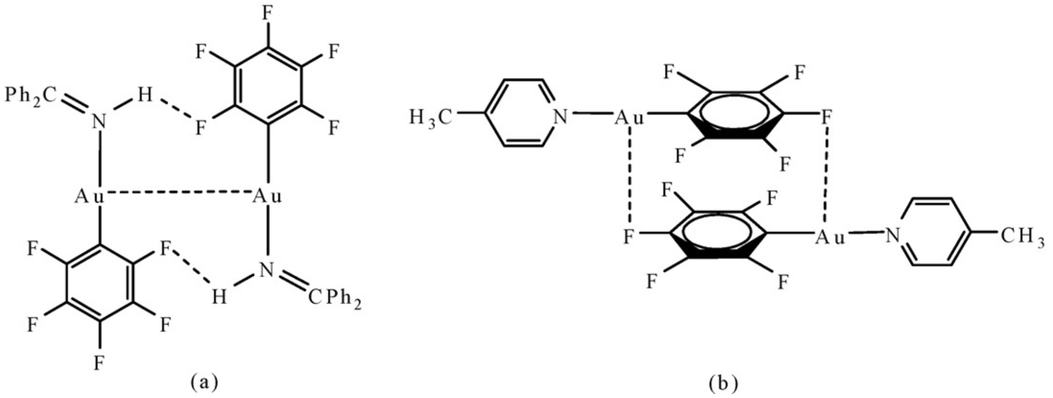
The Au–C distances are all very similar, ranging from 2.002(10) Å for L = N(H)=CPh_2 [88] to 1.992(6) Å for L = $Ph_2C_2N_2$ [90], and shorter than in complexes with other donor atoms, such as phosphorus or carbon, indicating a lower *trans* influence for the nitrogen donor ligands. The Au–N lengths are in the range 2.044(8)–2.081(8) Å and are comparable to the separations in gold(I) amine [92], imine [93,94] and amide [95] complexes (2.024(7)–2.0806 Å).

The benzophenoneimine derivative displays an interesting molecular packing, which reveal discrete dimers in an antiparallel conformation. Both Au···Au interactions (3.5884(7) Å) and N–H···F hydrogen bonds (H···F 2.75 Å, N–H···F 116°) are present within the dimeric units (see Fig. 7a) [88]. The gold atoms in the 4-methylthiazole derivative are involved in aurophilic interactions (Au–Au 3.345(1) Å) [71], while the other two compounds display no intermolecular Au···Au interactions, although the molecular packing of $[Au(C_6F_5)(3\text{-picoline})]$ involves an Au···F contact (Au···F distance of 3.507(4) Å) that links two molecules as shown in Fig. 7b [89].

The gold(III) complex $[Au(C_6F_5)_3(2\text{-amt})]$ can be obtained from $[Au(C_6F_5)_3(tht)]$ and 2-aminothiazoline using the same



Scheme 11.

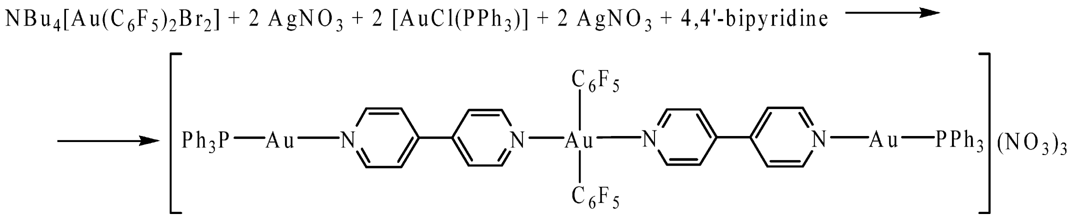


(a) (b)

Fig. 7. Dimers of $[Au(C_6F_5)L]$

synthetic procedure [91]. Its crystal structure shows a shorter Au^{III}–C bond length (2.016(2) Å) for the pentafluorophenyl groups *trans* to nitrogen than those *trans* to C_6F_5 (2.063(2) and 2.068(2) Å), confirming the stronger *trans* influence for carbon- than for nitrogen-donor ligands. The Au^{III}–N length of 2.0664(18) Å is in the range of Au^{I}–N distances (2.044(8)–2.081(8) Å) observed in the complexes commented above.

Finally, the trinuclear mixed-valence complex $[Au(C_6F_5)_2\{(4,4'\text{-bipy})Au(PPh_3)\}_2](NO_3)_3$ (bipy = 4,4′-bipyridine) [96] can be prepared by reaction of $[Au(C_6F_5)_2(NO_3)_2]$ and $[Au(PPh_3)(NO_3)]$ prepared in situ with 4,4′-bipyridine (1:2:2) (Eq. (13)), and multinuclear NMR research (^1H, ^1H–^1H COSY, ^{13}C, ^{19}F and ^{31}P) has been carried out to study this.



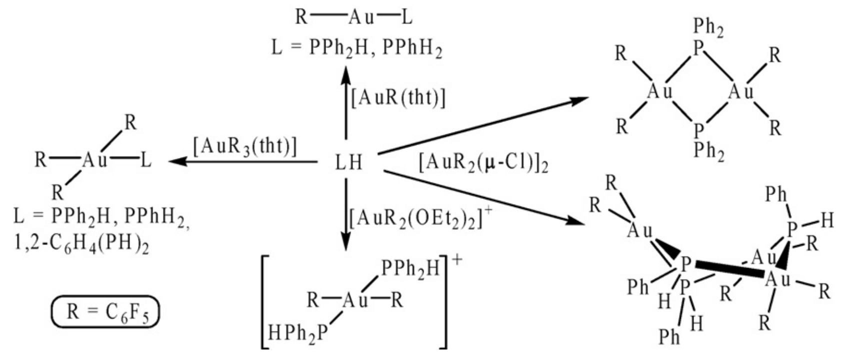
(13)

4.2. P-donor ligands

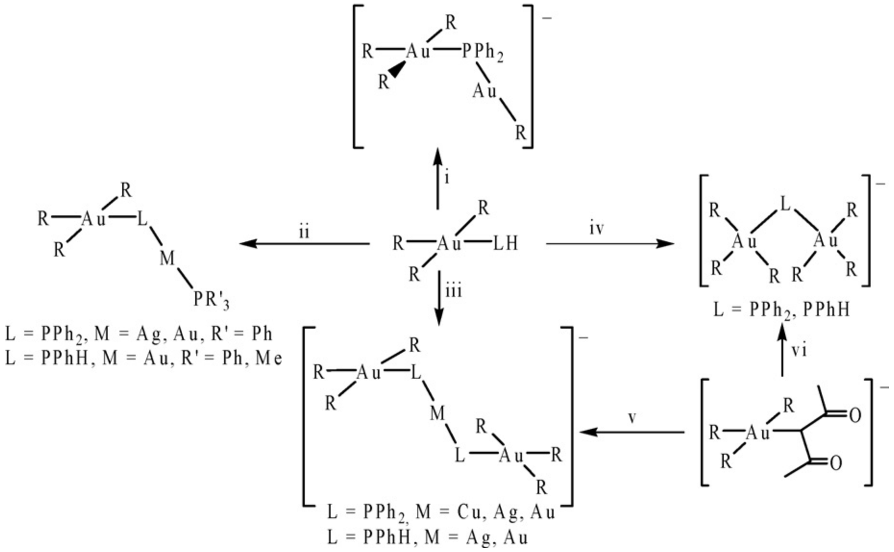
4.2.1. Primary and secondary phosphines and phosphides

The usual method for displacing the labile ligand tht by phosphorus donor ligands extensively employed with a variety of tertiary phosphines has also been used recently for the synthesis of pentafluorophenyl complexes containing primary or secondary phosphines, such as diphenylphosphine [97,98], phenylphosphine [99] or 1,2-diphosphinobenzene [100]. Thus, the gold(I) or gold(III) phosphino derivatives $[Au(C_6F_5)(LH)]$ (LH = PPh_2H, $PPhH_2$), $[Au(C_6F_5)_3(LH)]$ (LH = PPh_2H, $PPhH_2$, 1,2-$C_6H_4(PH_2)_2$) or *trans*-$[Au(C_6F_5)_2(PPh_2H)_2]ClO_4$ have been described, the latter showing a *trans* disposition of the ligands as its IR spectrum indicates [97] (see Scheme 12). These products, and mainly the gold(I) compounds, are moderately stable and can be easily deprotonated due to the high acidity of the phosphinic protons. Even each chlorine atom of $[Au_2(C_6F_5)_4(\mu\text{-}Cl)_2]$ can extract one proton when treated with PPh_2H or $PPhH_2$, and the cyclic di- or trinuclear phosphide derivatives $[Au(C_6F_5)_2(\mu\text{-}PPh_2)]_2$ [101] or $[Au(C_6F_5)_2(\mu\text{-}PPhH)]_3$ [99] are isolated.

The latter still contains acidic protons and also reacts with $[Au(acac)(PPh_3)]$ to afford the tetranuclear

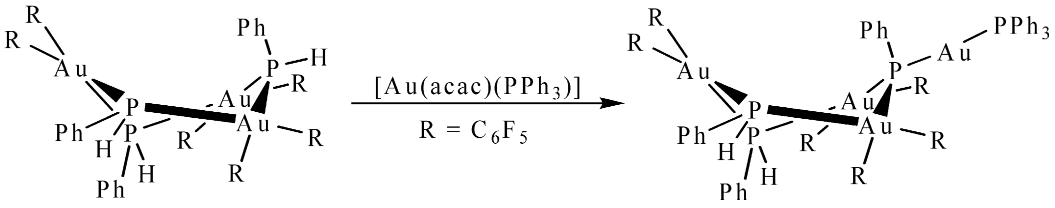


Scheme 12.



Scheme 13. $R = C_6F_5$; (i) [AuR(tht)] + NBu_4(acac); (ii) [Au(acac)(PPh_3)], [Ag(TfO)(PPh_3)] + NBu_4(acac) or [AuCl(PMe_3)] + Tl(acac); (iii) 1/2 PPN[$Au(acac)_2$], 1/2 $AgClO_4$ + PPN(acac) or 1/2 [$Cu(NCMe)_4$]TfO + PPN(acac); (iv) [AuR_3(tht)] + NBu_4(acac); (v) 1/2 [$Au(PPh_2H)_2$]TfO; (vi) [$AuR_3(PPh_2H)$].

phosphide/phosphodiide derivative $[\{Au(C_6F_5)_2(\mu\text{-}PPhH)\}_2\{Au(C_6F_5)_2(\mu_3\text{-}PPh)Au(PPh_3)\}]$ [99] (Eq. (14)). Both the di- and trinuclear cyclic compounds have been structurally characterized, displaying, respectively, a tetra- or hexanuclear ring of alternating square-planar gold(III) and tetrahedral phosphorus atoms, the latter in a twisted boat conformation.



(14)

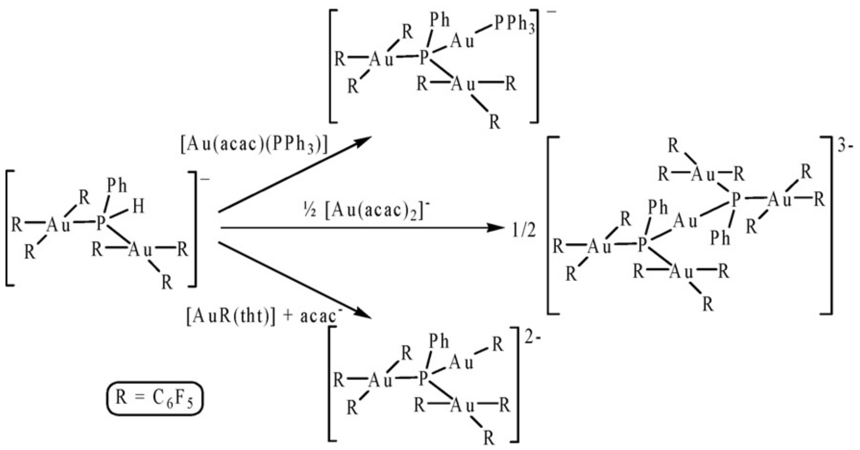
The low stability of the gold(I) phosphino derivatives of PPh_2H and $PPhH_2$ means that they cannot be used as starting complexes, but the gold(III) products are stable enough to study their reactivity against 11 group metal complexes in the presence of a basic anion. Thus, freshly prepared solutions of $[Au(C_6F_5)_3(LH)]$ (LH = PPh_2H, $PPhH_2$) react with equimolecular amounts of Au^{III} or M^I (M = Ag, Au) reagents in the presence of acetylacetonate to yield dinuclear species of formula $[\{Au(C_6F_5)_3\}_2(\mu\text{-}L)]^-$, $[Au(C_6F_5)_3(\mu\text{-}L)M(PR'_3)]$ ($L = PPh_2$, M = Ag, Au, R′ = Ph; L = PPhH, M = Au, R′ = Ph, Me) or $[Au(C_6F_5)_3(\mu\text{-}PPh_2)Au(C_6F_5)]^-$ [97,99,101] as shown in Scheme 13.

The trinuclear compounds $PPN[\{Au(C_6F_5)_3(\mu\text{-}L)\}_2M]$ ($L = PPh_2$, M = Cu, Ag, Au; L = PPhH, M = Ag, Au), also obtained from $[Au(C_6F_5)_3(LH)]$, contain perfectly linear M^I centers bonded to two phosphido gold(III) fragments [98,99]. The X-ray crystal structure determinations were carried out for the silver(I) and gold(I) diphenylphosphido species [98], enabling their covalent radii to be compared, and revealing that gold is smaller than silver in 0.07 Å, confirming the results obtained by Schmidbaur [102]. An alternative synthesis strategy consisted in the use of $[Au(C_6F_5)_3(acac)]^-$ as gold(III) precursor, as shown in Scheme 13.

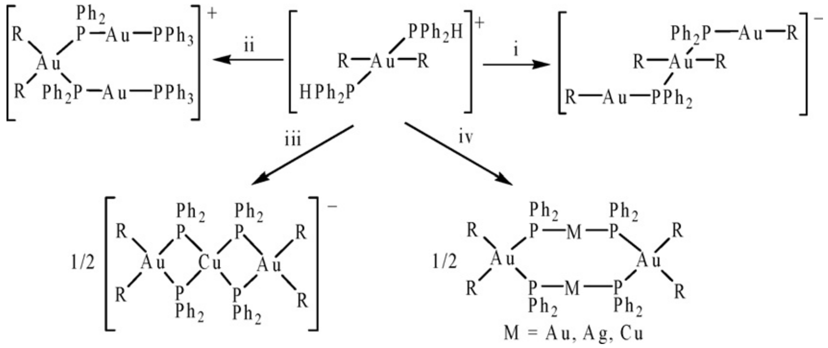
The phenylphosphide derivative $PPN[\{Au(C_6F_5)_3\}_2(\mu\text{-}PPhH)]$ also reacts with similar gold(I) precursors to afford higher nuclearity phosphodiide anions, such as the trinuclear $[\{Au(C_6F_5)_3\}_2(\mu_3\text{-}PPh)Au(PPh_3)]^-$, $[\{Au(C_6F_5)_3\}_2(\mu_3\text{-}PPh)Au(C_6F_5)]^{2-}$ or the pentanuclear trianion $[\{(Au(C_6F_5)_3)_2(\mu_3\text{-}PPh)\}_2Au]^{3-}$ [99] (Scheme 14). Some other phosphodiides, such as $[\{Au(C_6F_5)_3\}(\mu_3\text{-}PPh)\{Au(PPh_3)\}_2]$ or $[\{Au(C_6F_5)_3\}(\mu_3\text{-}PPh)\{Au(C_6F_5)\}\{Au(PPh_3)\}]^-$, have also been synthesized using the same strategy [99].

Similarly, starting from *trans*-$[Au(C_6F_5)_2(PPh_2H)_2]ClO_4$, the trinuclear derivatives *trans*-$NBu_4[Au(C_6F_5)_2\{(\mu\text{-}PPh_2)Au(C_6F_5)\}_2]$, *cis*-$[Au(C_6F_5)_2\{(\mu\text{-}PPh_2)Au(PPh_3)\}_2]ClO_4$ or $PPN[\{Au(C_6F_5)_2(\mu\text{-}PPh_2)_2\}_2Cu]$, which contain two (the first two) or four (the latter) phosphido bridging ligands, have been obtained [97]. A series of tetranuclear neutral complexes $[Au(C_6F_5)_2(\mu\text{-}PPh_2)_2M]_2$ (M = Cu, Ag, Au) can also be isolated by reaction of the same gold(III) starting material with M(I) salts in the presence of acetylacetonate as deprotonating agent (2:1), as shown in Scheme 15.

Furthermore, reaction of the mixed Au^{III}/Ag^I diphenylphosphide complex $[Au(C_6F_5)_2(\mu\text{-}PPh_2)_2Ag]_2$ with an equimolecular amount of $[AgCl(PPh_3)]$ leads to the formal insertion of the latter into the starting complex, yielding the



Scheme 14.



Scheme 15. R = C_6F_5; (i) 2 [AuR(tht)] + 2 NBu4(acac); (ii) 2 $[Au(acac)(PPh_3)]$; (iii) 1/2 $[Cu(NCMe)_4]TfO$ + 2 PPN(acac); (iv) $[Cu(NCMe)_4]TfO$ + 2 PPN(acac), $Ag(OClO_3)$ + 2 PPN(acac) or $PPN[Au(acac)_2]$.

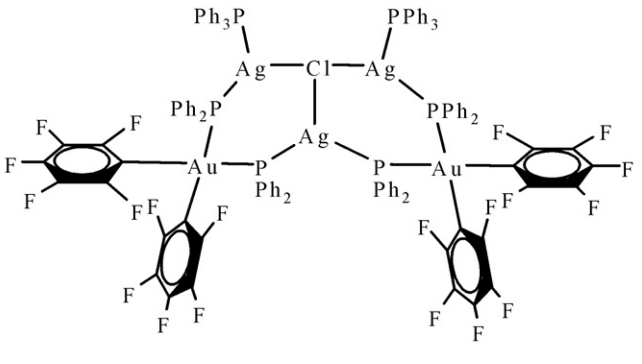
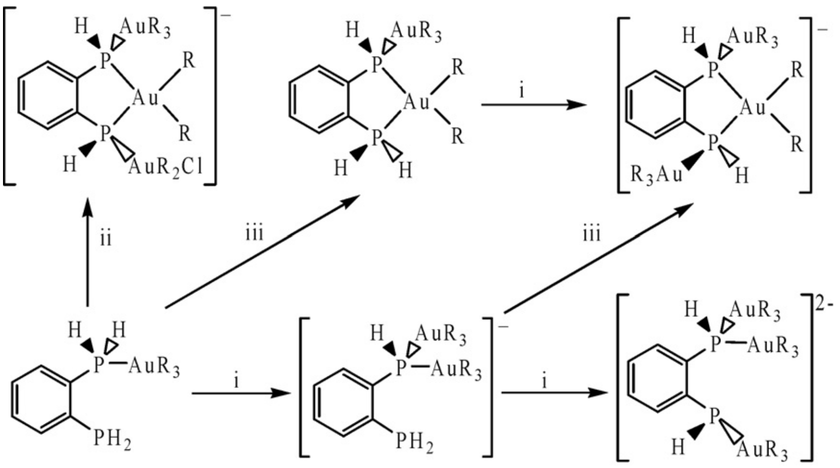


Fig. 8. Structure of $[\{Au(C_6F_5)_2\{(PPh_2)AgPPh_3\}(PPh_2)\}_2(Ag)(Cl)]$

pentanuclear derivative $[\{Au(C_6F_5)_2\{(\mu\text{-}PPh_2)AgPPh_3\}(\mu\text{-}PPh_2)\}_2(\mu\text{-}Ag)(\mu_3\text{-}Cl)]$ [103]. This compound displays an unusual perfectly planar T-frame μ_3-Cl bridging the three silver atoms [Ag–Cl–Ag 91.66(4) and 176.68(8)°] (see Fig. 8). Surprisingly, this compound is also obtained by treatment of *trans*-$[Au(C_6F_5)_2(PPh_2H)_2]ClO_4$ with $[Ag(TfO)(PPh_3)]$ (TfO = trifluoromethylsulfonate) and AgTfO (2:2:1) in the presence of PPN(acac) and PPNCl [103].

A number of cyclic or non-cyclic gold(III) phosphino-phosphides or diphosphides were synthesized from 1,2-diphosphinobenzene (Scheme 16) [100]. The diphosphino complex $[\{Au(C_6F_5)_3\}(1,2\text{-}PH_2C_6H_4PH_2)]$ or the phosphane–phosphide $[\{Au(C_6F_5)_3\}_2(1,2\text{-}PHC_6H_4PH_2)]^-$ react with suitable pentafluorophenylgold(III) precursors in the presence of free or coordinated acetylacetonate to afford the di- or trinuclear species shown in Scheme 16. In some of these reactions, the migration of one $Au(C_6F_5)_3$ group from one phosphorus to the other was observed. In the case of *trans*-$[\{Au(C_6F_5)_3\}(1,2\text{-}PHC_6H_4PH)\{Au(C_6F_5)_2Cl\}\{\mu\text{-}Au(C_6F_5)_2\}]^-$, both the acetylacetonate and one of the chlorine atoms of $[Au(\mu\text{-}Cl)(C_6F_5)_2]_2$ act as deprotonating agents in a reaction that occurs with the breaking of the dinuclear compound and that leads to a complex with three different pentafluorophenylgold(III) fragments, which has been confirmed by its crystal structure.

$[\{Au(C_6F_5)_3\}_2(1,2\text{-}PHC_6H_4PH_2)]^-$ has also been shown to be a useful starting material for the synthesis of mixed Au^{III}/M^I (M = coinage metal) diphosphide or diphosphodiide compounds using a similar synthetic strategy [100]. Thus, its reaction with phosphino- or pentafluorophenylgold(I) or silver(I) complexes in the presence of the same deprotonating agent leads to trinuclear diphosphides displaying a tricoordinated gold(I) or silver(I) center (see Scheme 17). The bridging chlorine atom of $[\{Au(PPh_3)\}_2(\mu\text{-}Cl)]^+$ is able to extract one phosphinic proton from $[\{Au(C_6F_5)_3\}_2(1,2\text{-}PHC_6H_4PH_2)]^-$ to yield the tetranuclear diphosphodiide complex $[\{Au(C_6F_5)_3\}(AuPPh_3)(1,2\text{-}$



Scheme 16. R = C_6F_5; (i) $[AuR_3(tht)] + acac^-$; (ii) $[Au(\mu\text{-}Cl)R_2]_2 + acac^-$; (iii) $[AuR_2(acac)]$.

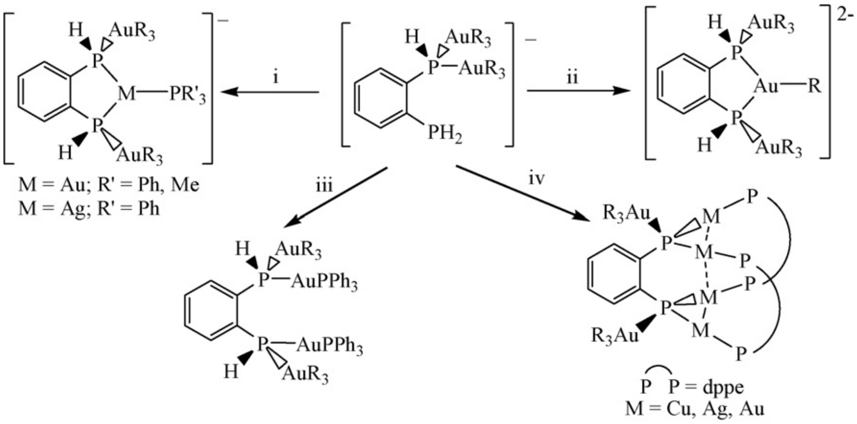
$PHC_6H_4PH)\{Au(C_6F_5)_3\}(AuPPh_3)]$. As in other cases, reaction takes place with the concomitant migration of one $Au(C_6F_5)_3$ group from one phosphorus to the other, leading to a more symmetric product. Lastly, the hexanuclear diphosphodiides $[\{Au(C_6F_5)_3\}(1,2\text{-}PC_6H_4P)\{Au(C_6F_5)_3\}\{\mu\text{-}M(dppe)M\}_2]$ (M = Cu, Ag, Au) were prepared in good yields using similar procedures [100].

The crystal structures of the hexanuclear Au^{III}/Au^{I} and Au^{III}/Ag^{I} species were determined [100], showing discrete molecules consisting of a 16-membered bicycle formed by the *ipso* carbon atoms and both phosphorus of the 1,2-diphosphodiidebenzene ligand and two M(dppe)M units, with each phosphorus of the diphosphodiide also bonded to a tris(pentafluorophenyl)gold(III) unit. An important feature in these structures is the presence of intramolecular $M^{I}\cdots M^{I}$ contacts of 2.9385(5), 3.0273(5) and 3.1105(5) Å for M = Au or 2.9215(15), 2.9822(16) and 3.0514(16) Å for M = Ag.

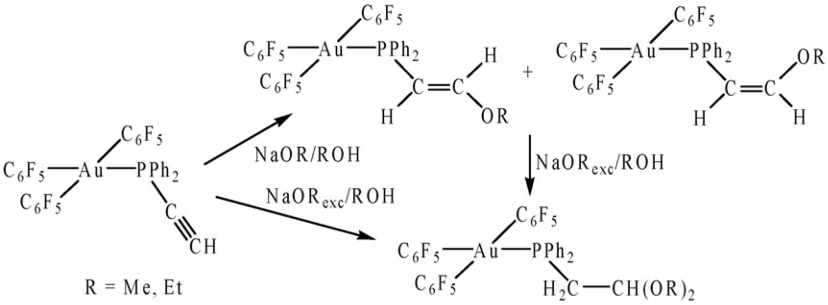
Probably thanks to the stabilizing effect of the perfluorophenyl groups, the crystal structures of many phosphidegold derivatives (14) has been established [97-101,103]. The comparison of the Au^{III}–C distances *trans* to phosphide (average 2.073 Å) and *trans* to pentafluorophenyl (average 2.061 Å) indicates a stronger *trans* influence for phosphide ligands than for the carbon donor group. The M^{I}–P lengths *trans* to phosphide [average 2.323 (M = Au), 2.400 Å (M = Ag)] are generally longer than those *trans* to phosphine [average 2.305 (M = Au), 2.387 Å (M = Ag)] are in accordance with a stronger *trans* influence for phosphide groups than for phosphines. The Au^{III}–P–M angles are generally wider than expected in a tetrahedral environment for phosphorus atoms, and avoid the presence of intermolecular $Au^{III}\cdots M$ interactions.

4.2.2. *Tertiary phosphines and derivatives*

4.2.2.1. Monophosphines. A large number of mononuclear gold(I) or gold(III) complexes with general formula $[Au(C_6F_5)L]$ (L = TPA (TPA = 1,3,5-triaza-7-phosphaadamantane) [77], $PPh_2C{\equiv}CH$ [104], $PPh_2C({=}S)N(H)Me$ [105], PPh_2CH_2SPh [106], $PPh_2(2\text{-}C_6H_4OH)$ [107], $PPh_2(2\text{-}C_6H_4OSiMe_3)$ [107]) or $[Au(C_6F_5)_3L]$ (L = TPA [77], $PPh_2(2\text{-}C_6H_4SH)$ [108], $PPh_2(2\text{-}C_6H_4NH_2)$ [109] and $PPh_2C{\equiv}CH$ [110]) have recently been prepared by rapid displacement of the weakly coordinated tetrahydrothiophene ligand from the precursor with the free phosphorus donor ligand.



Scheme 17. R = C_6F_5; (i) $[Au(acac)(PPh_3)]$ or $[AuCl(PMe_3)] + Tl(acac)$ or $[Ag(TfO)(PPh_3)] + PPN(acac)$; (ii) $[AuR(tht)] + acac^-$; (iii) $[\{Au(PPh_3)\}_2(\mu\text{-}Cl)]^+$; (iv) 2 $[(AuCl)_2(dppe)]$ + 4 $Ag(OClO_3)$ + 3 PPN(acac) or 2 $[M_2(dppe)](ClO_4)_2$ (M = Ag, Cu) + 3 PPN(acac).



Scheme 18.

The molecular packing of [Au(C_6F_5)($PPh_2C{\equiv}CH$)] involves an Au···H contact from the acidic alkynyl proton (Au···H distance of 3.07 Å, C–H–Au angle of 143°) that links the molecules by translation parallel to the *a* axis [104].

Other gold(III) complexes of the same type can be obtained by alternative methods, such as the double addition of alcohol to the acetylene phosphine fragment of [Au(C_6F_5)$_3$($PPh_2C(CH)$)] by reaction with sodium alkoxides to obtain [Au(C_6F_5)$_3$($PPh_2CH{=}CHOR$)] or [Au(C_6F_5)$_3${$PPh_2CH_2CH(OR)_2$}] (R = Me, Et) [110], as shown in Scheme 18.

The solid-state structures of the tris(pentafluorophenyl) derivatives of TPA [77], $PPh_2(2\text{-}C_6H_4SH)$ [108] and $PPh_2CH_2CH(OMe)_2$ [110] show Au–P distances that are considerably shorter for the TPA complex (2.3285(10) and 2.3228(10) Å) than those found in the other two phosphine complexes (2.3884(16) and 2.3692(8) Å, respectively); this shortening is likely due to the low steric bulk of the TPA ligand. The Au–C bond lengths for the C_6F_5 groups *trans* and *cis* to the phosphine are almost equal in the three structures ranging from 2.057(5) to 2.079(2) Å.

The related bis(pentafluorophenyl) phosphine compounds *cis*-[Au(C_6F_5)$_2$Cl{$PPh_2(2\text{-}C_6H_4NH_2)$}] [109], *cis*-[Au($C_6F_5$)$_2$($PPh_2CH_2SPh$)$_2$]$ClO_4$ [111] and *trans*-[Au(C_6F_5)$_2$(TPA)$_2$]TfO [77] can also be synthesized by chlorine bridge rupture or displacement reactions. The *cis* arrangement of the aryl groups in the former two has been confirmed by X-ray diffraction studies; both display rather long Au–P bonds (2.3818(14)–2.3990(15) Å) if compared with other phosphinogold(III) complexes and the greater *trans* influence of 2-diphenylphosphinoaniline compared with chlorine is reflected in the Au–C distances of 2.038(4) and 2.068(4) Å in *cis*-[Au(C_6F_5)$_2$Cl{$PPh_2(2\text{-}C_6H_4NH_2)$}] [109]. In this molecular structure, the amine group forms an intramolecular hydrogen bond to a fluorine atom (Fig. 9).

4.2.2.2. Diphosphines. When diphosphines are employed in substitution reactions with [Au(C_6F_5)$_n$(tht)] (n = 1, 3), the resulting product mainly depends on the number of pentafluorophenyl groups attached to gold. Thus, while the gold(I) reagent always leads to dinuclear species [{Au(C_6F_5)}$_2$(L,L)] [82,112–114] whatever the molar ratio is, the reaction with the tris(pentafluorophenyl) complex usually affords the monodentate [Au(C_6F_5)$_3$(L,L)] [82,112,113] even if excess of [Au(C_6F_5)$_3$(tht)] is used (see Scheme 19). Only in the cases of $(1,2\text{-}PPh_2NH)_2\text{-}4\text{-}MeC_6H_3$, $1,2\text{-}(PPh_2NH)_2C_6H_4$ [82] or $PPh_2C{\equiv}CPPh_2$ [114] has the use of two moles of the gold(III) starting material resulted in dinuclear derivatives [{Au(C_6F_5)$_3$}$_2$(L,L)].

Similarly, the reaction of [Au(C_6F_5)$_2$(μ-Cl)]$_2$ with vdpp [vdpp = vinylidenebis(diphenylphosphine) $(PPh_2)_2C{=}CH_2$] leads to [Au(C_6F_5)$_2$Cl{$PPh_2C({=}CH_2)PPh_2$}] [115]. The coordination of the diphosphine to a gold(III) center strongly activates the carbon–carbon double bond, and this complex easily undergoes Michael-type additions with different nucleophiles. Treatment of [Au(C_6F_5)$_2$Cl{$PPh_2C({=}CH_2)PPh_2$}] with Ag($OClO_3$) in diethyl or diisopropyl ether led surprisingly to [Au(C_6F_5)$_2${$(PPh_2)_2CHCH_2OR'$}]ClO_4 (R′ = Et, ^{i}Pr), probably the result of adding a molecule of R′ to the C=C bond in [Au(C_6F_5)$_2${$(PPh_2)_2C{=}CH_2$}]ClO_4, a product that cannot be isolated due to its great reactivity [115]. The same complexes are also obtained when the free diphosphine is treated with [Au(C_6F_5)$_2$(OR′)$_2$]ClO_4 (R′ = Et, ^{i}Pr) in the same solvents (Scheme 20). Protonation of the methanide complexes [Au(C_6F_5)$_2${$(PPh_2)_2CCH_2Nu$}] (Nu = OEt, acac) with $HClO_4$ also affords the diphosphino derivatives [Au(C_6F_5)$_2${$(PPh_2)_2CHCH_2Nu$}]ClO_4 [115].

Although displacement of tht is the most common synthetic approach, digold(I) products [{(C_6F_5)Au}$_2${μ-2,2′-$(PR_2C_6H_4)_2$}] (R = Ph, Et) are obtained after prolonged heating in toluene of gold(II) complexes [Au(C_6F_5)(μ-2-$PR_2C_6H_4$)]$_2$ in a reaction that takes place with a rearrangement of ligands and the carbon–carbon coupling of the $PR_2C_6H_4$ units, as shown in Eq. (15) [116]. Nevertheless, this reaction occurs with the simultaneous formation of a small amount of zwitterionic heterovalent complexes [Au{μ-2,2′-$(PR_2C_6H_4)$}$_2$Au(C_6F_5)$_2$].

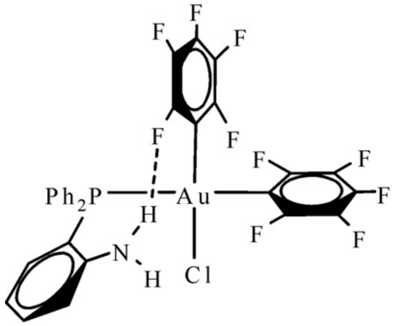
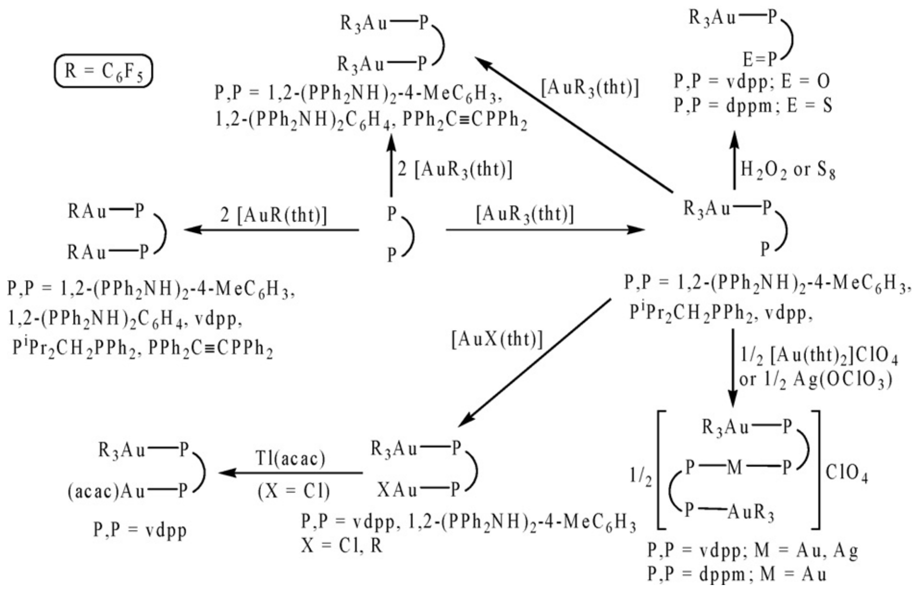
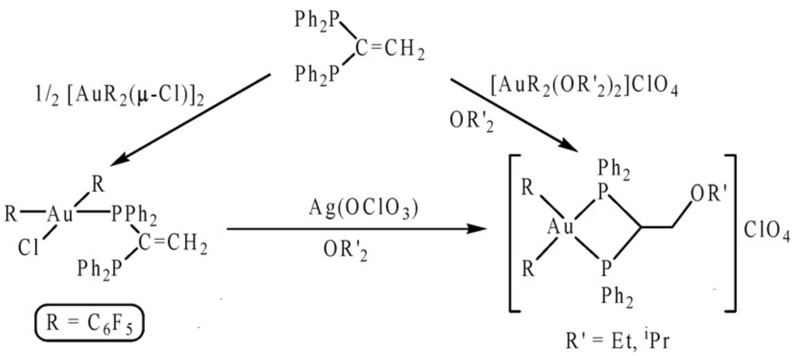


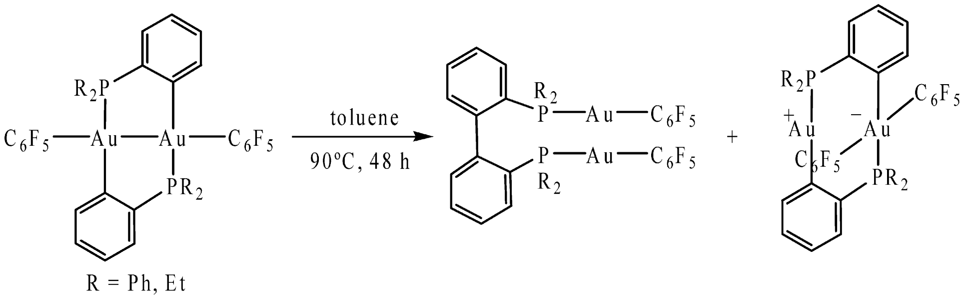
Fig. 9. Structure of Au(C_6F_5)$_2$Cl{$PPh_2(2\text{-}C_6H_4NH_2)$}]



Scheme 19.



Scheme 20.



(15)

One aminic proton can be removed from $[\{Au(C_6F_5)_n(PPh_2NH)\}_2\text{-}4\text{-}RC_6H_3]$ ($n = 1$, 3; R = Me, H) by addition of the deprotonating agent $NBu_4(acac)$ yielding the dinuclear anionic complexes $NBu_4[\{Au(C_6F_5)_n(PPh_2N)\}\{Au(C_6F_5)_n(PPh_2NH)\}\text{-}4\text{-}RC_6H_3]$ ($n = 1$, 3; R = Me, H) [82] and the further auration of the benzene gold(III) derivative with $[Au(OClO_3)(PPh_3)]$ leads to a trinuclear complex containing a P,P,N-tridentate ligand, as confirmed by X-ray diffraction methods.

In some $[Au(C_6F_5)_3(L,L)]$ complexes, the oxidation or sulfuration of uncoordinated phosphorus giving $[Au(C_6F_5)_3\{PPh_2C(=CH_2)PPh_2O\}]$ [113] or $[Au(C_6F_5)_3(PPh_2CH_2PPh_2S)]$ [85] has been reported (see Scheme 19). Coordination of the free P atom to Au(I) or Ag(I) by treatment with the adequate metal precursor with labile ligands results in the formation of di- or trinuclear species $[Au(C_6F_5)_3(L,L)AuX]$ (P,P=$(PPh_2)_2C{=}CH_2$, 1,2-$(PPh_2NH)_2$-4-MeC_6H_3; X = Cl, C_6F_5) [82,113] or $[\{Au(C_6F_5)_3(L,L)\}_2M]ClO_4$ (P,P=$(PPh_2)_2C{=}CH_2$, M = Au, Ag; P,P = dppm, M = Au) [113,117]. Finally, the treatment of $[Au(C_6F_5)_3\{PPh_2C(=CH_2)PPh_2\}AuCl]$ with Tl(acac) leads

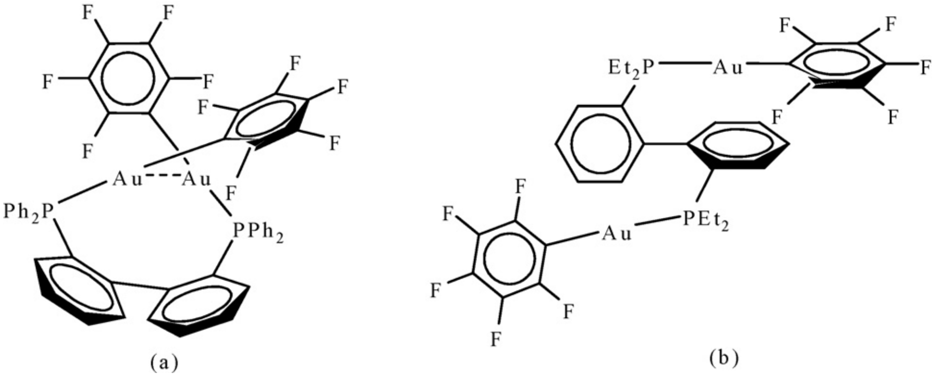


Fig. 10. Structure of $[\{Au(C_6F_5)\}_2(L,L)]$

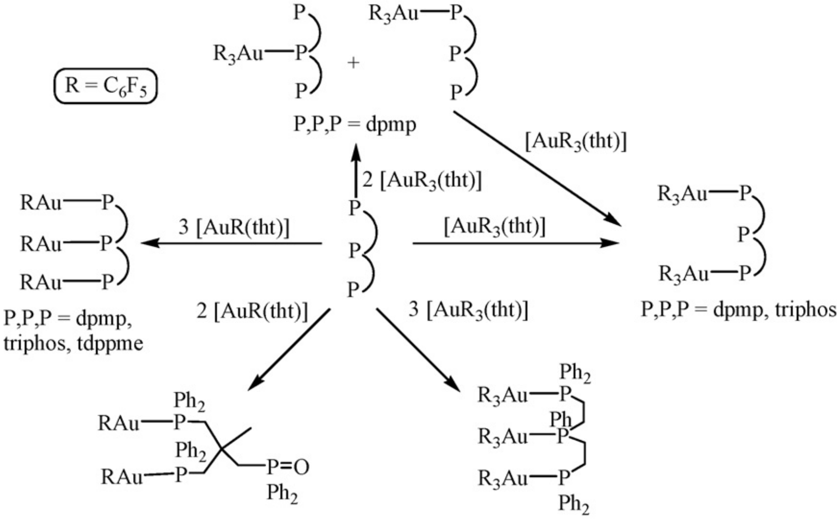
to the substitution of the chlorine atom with the concomitant precipitation of TlCl (Scheme 19) instead of nucleophilic addition to the C=C bond [113].

The crystal structures of the gold(I) compounds $[\{Au(C_6F_5)\}_2(L,L)]$ (L,L = 1,2-$(PPh_2NH)_2$-4-MeC_6H_3] [82], $P^iPr_2CH_2PPh_2$ [112], $PPh_2C(CPPh_2$ [114] and 2,2′-$(PR_2C_6H_4)_2$ (R = Ph, Et) [116]) show Au–C and Au–P distances ranging from 2.02(1) to 2.056(9) Å and from 2.263(2) to 2.285(3) Å, respectively. The orientation and rigidity of the ligand backbone are responsible for the presence or absence of intramolecular aurophilic contacts, which are only observed for $P^iPr_2CH_2PPh_2$ (Au···Au 3.0926(3) Å) and 2,2′-$(PPh_2C_6H_4)_2$ (Au···Au 3.0688(8) Å) and even very similar complexes, such as the 2,2′-$(PR_2C_6H_4)_2$ derivatives, can display noticeable differences depending on the torsion around the central C–C bond (Fig. 10).

The solid-state structures of three Au^{III}/Au^{I} compounds namely $[\{Au(C_6F_5)_3(PPh_2NH)\}_2$-4-$MeC_6H_3]$, $[\{Au(C_6F_5)_3\}_2(PPh_2NH)C_6H_4\{N(AuPPh_3)PPh_2\}]$ [82] and $[Au(C_6F_5)_3\{PPh_2C(=CH_2)PPh_2\}Au(C_6F_5)]$ [113], have also been established. The comparison of the Au^{III}–C (2.051(6)–2.088(9) Å) and Au^{III}–P (2.346(2)–2.23829(15) Å) bond lengths with the Au^{I}–C (2.02(1)–2.056(9) Å) and Au^{I}–P (2.2404(16)–2.285(3) Å) separations in the diphosphine complexes structurally characterized have again revealed an unexpected tendency of longer Au–P and Au–C distances to gold(III) than to gold(I) (see above).

4.2.2.3. Triphosphines. As in the case of diphosphines, higher nuclearity complexes have been obtained in the reaction of triphosphines with $[Au(C_6F_5)(tht)]$ than with $[Au(C_6F_5)_3(tht)]$, the former leading to trinuclear derivatives of the type $[\{Au(C_6F_5)\}_3(\mu_3\text{-}L,L,L)]$, as described for $PPh(CH_2CH_2PPh_2)_2$ (triphos) [118], $PPh(CH_2PPh_2)_2$ (dpmp) [119] or $(PPh_2CH_2)_3CCH_3$ (tdppme) [120]. The reaction of tdppme with $[Au(C_6F_5)(tht)]$ in a 1:2 molar ratio occurs with the concomitant oxidation of one of the phosphorus to afford the dinuclear complex $[\{Au(C_6F_5)\}_2\{\mu\text{-}(PPh_2CH_2)_2C(CH_3)CH_2PPh_2O]$ (see Scheme 21) and no mononuclear gold(I) product can be prepared from the triphoshine [120].

In contrast, if the gold(III) precursor is used in the reaction with dpmp or tdppme (1:1) complexes $[Au(C_6F_5)_3(L,L,L)]$, which display phosphine as monodentate, are isolated [119,120]. $^{31}P\{^1H\}$ NMR data in $CDCl_3$ even at −60 °C show that the dpmp derivative is a mixture of two isomers because of



Scheme 21.

the coordination of gold to the central or the lateral phosphorus, although it would appear that only the first isomer crystallizes at −18 °C. The addition of a second equivalent of $[Au(C_6F_5)_3(tht)]$ to $[Au(C_6F_5)_3(dpmp)]$ or the same reaction in 2:1 ratio evolves cleanly to the formation of a unique derivative, $[\{Au(C_6F_5)_3\}_2(\mu\text{-dpmp})]$, which presumably displays the $Au(C_6F_5)_3$ fragments coordinated to the most external phosphorus [119] (see Scheme 21). This complex reacts with $[AuX(tht)]$ ($X = Cl, C_6F_5$) to give the mixed-valence $Au^I–Au^{III}–Au^I$ complexes $[\{Au(C_6F_5)_3\}_2(\mu_3\text{-dpmp})AuX]$ [119].

In contrast, the use of a ligand with longer hydrocarbon chains, such as triphos, leads to the synthesis of both the di- and trinuclear complexes $[\{Au(C_6F_5)_3\}_n(triphos)]$ ($n = 2, 3$) [118]. $^{31}P\{^1H\}$ NMR data seem to indicate that the dinuclear product is a mixture of three isomers. In the crystal structure of the trinuclear product, the structure of the ligand allows the three bulky $Au(C_6F_5)_3$ units to be coordinated at the same time, and shows very long Au–Au distances (the shortest one 7.095 Å), which precludes any form of metal–metal bonding.

It has been observed that the dpmp and triphos gold(I) derivatives are luminescent at low temperature in solid state [118,119], which is usually related to the presence of $Au^I\cdots Au^I$ interactions, although in these cases no X-ray crystal structure were determined to confirm the presence of such interactions. Even $[\{Au(C_6F_5)_3\}_3(triphos)]$ [118] shows the same optical properties, which is not usual in gold(III) derivatives.

A couple of complexes containing a triphoshine as bidentate chelate, namely $[Au(C_6F_5)_2\{(PPh_2CH_2)_2C(CH_3)CH_2PPh_2\}]Cl$ and $[Au(C_6F_5)_2\{(PPh_2)_2CHPPh_2\}]BF_4$, have been obtained by reaction of tdppme with $[Au(C_6F_5)_2(\mu\text{-Cl})]_2$ [120] or by protonation of the methanide derivative $[Au(C_6F_5)_2\{(PPh_2)_2CPPh_2\}]$ with HBF_4 [121].

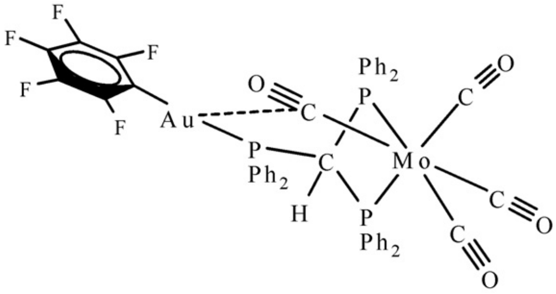
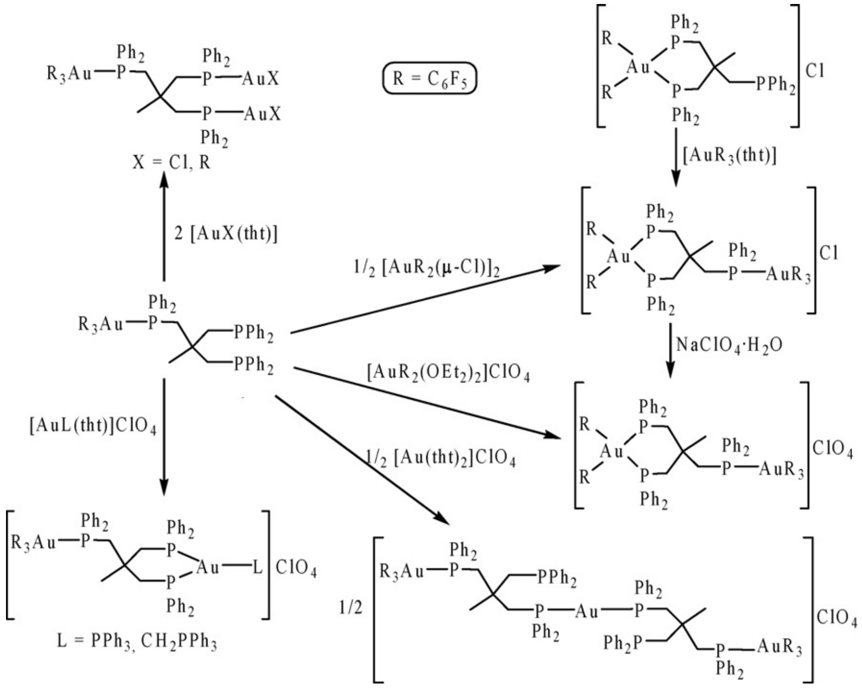


Fig. 11. Structure of $[(CO)_4Mo\{(PPh_2)_2CHPPh_2\}Au(C_6F_5)]$

The reactivity of the mononuclear tdppme products $[Au(C_6F_5)_3\{PPh_2CH_2C(CH_3)(CH_2PPh_2)_2\}]$ $[Au(C_6F_5)_2\{(PPh_2CH_2)_2C(CH_3)CH_2PPh_2\}]Cl$, which still present two or one free phosphorus, respectively, has been studied. Di- or trinuclear gold(III) or mixed-valence complexes, which contain the ligand in different coordination modes, have thus been synthesized *via* displacement reactions with gold(I) or gold(III) reagents as schematized in Scheme 22 [120].

Finally, the heterometal complexes $[(CO)_4M\{(PPh_2CH_2)_2C(CH_3)CH_2PPh_2\}Au(C_6F_5)_nX]$ ($M = Mo, W$; $n = 0$, $X = C_6F_5$; $n = 2$, $X = Cl, C_6F_5$) or $[(CO)_4M\{(PPh_2)_2CHPPh_2\}Au(C_6F_5)]$ ($M = Cr, Mo, W$) have also been prepared from $[(CO)_4M\{(PPh_2CH_2)_2C(CH_3)CH_2PPh_2\}]$ or $[(CO)_4M\{(PPh_2)_2CHPPh_2\}]$, respectively, by ligand-displacement or bridge-cleavage [122,123]. The solid-state structure of one of the latter shows the ligand bridging a $Mo(CO)_4$ and a $Au(C_6F_5)$ unit and acting as chelating ligand at molybdenum (Fig. 11). The parallel alignment of the linear gold



Scheme 22.

system with one of the carbonyl groups, with a torsion angle C–Mo···P–Au of 3°, allows the Au···C contact of 3.441 Å [123].

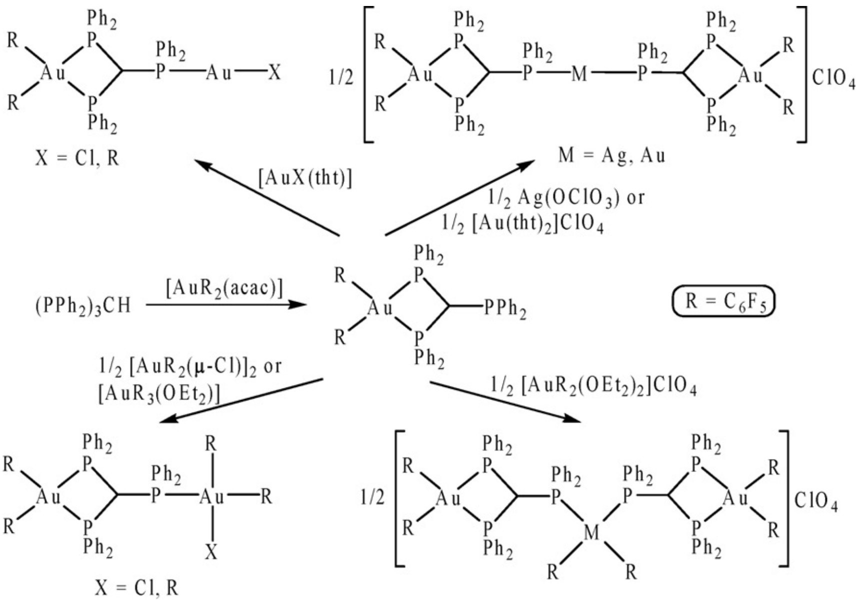
4.2.2.4. Phosphino methanides. As can be deduced from the large number of phosphino-methanide and methanediide derivatives already known, mainly of bis(diphenylphosphino)methane, the formation of cyclic methanides is more likely than the preparation of open ones, probably due to the stabilization produced by the delocalization of electronic density through the ring [124]. As in the case of phosphide derivatives, the most effective and simple way to synthesize phosphinomethanide complexes consists in the use of acetylacetonate, both uncoordinated and bonded to a gold atom, as base. Thus, the reaction of tris(diphenylphosphino)methane with $[Au(C_6F_5)_2(acac)]$ produces methanide $[Au(C_6F_5)_2\{(PPh_2)_2CPPh_2\}]$, which displays a four-membered metallacycle. The presence of a free phosphorus allows the coordination of new metallic fragments and, consequently, the di- or trinuclear species $[Au(C_6F_5)_2\{(PPh_2)_2CPPh_2\}AuX(C_6F_5)_n]$ ($n = 0$, 2; X = Cl, C_6F_5), $[\{Au(C_6F_5)_2\{(PPh_2)_2CPPh_2\}\}_2M]ClO_4$ (M = Ag, Au) or $[\{Au(C_6F_5)_2\{(PPh_2)_2CPPh_2\}\}_2Au(C_6F_5)_2]ClO_4$ can be isolated from its reaction with the appropriate metal precursor in 1:1 or 2:1 molar ratio, respectively [121] (Scheme 23). The methanide CP_3 system is so stable that the new metal atoms are always incorporated in the phosphorus, and even with an excess of metal reagent the methanide carbon atom remains uncoordinated.

The related methanide complexes $NBu_4[M(CO)_4\{(PPh_2)_2CPPh_2\}Au(C_6F_5)]$ (M = Cr, Mo, W) can also been prepared by reaction of $[M(CO)_4\{(PPh_2)_2CHPPh_2\}Au(C_6F_5)]$ with $NBu_4(acac)$ [123]. In the crystal structures of $[Au(C_6F_5)_2\{(PPh_2)_2CPPh_2\}]$, $[Au(C_6F_5)_2\{(PPh_2)_2CPPh_2\}AuCl]$ or $NBu_4[Mo(CO)_4\{(PPh_2)_2CPPh_2\}Au(C_6F_5)]$, the coordination of gold(III) or molybdenum(0) is slightly distorted from square-planar or octahedral, respectively, probably imposed by the chelate ligand, with a P–M–P angle of 70.1(2), 70.78(7) or 65.14(5)°. The P–C distances (1.74(2)–1.79(2) Å, 1.742(7)–1.770(7) Å and 1.761(6)–1.775(6) Å, respectively) are similar and shorter than in free $(PPh_2)_3CH$ [125] (1.867(1)–1.877(1) Å) or in other phosphine derivatives. This can be attributed to a degree of multiple P–C bonding in the methanide ligand, which is also consistent with a sp^2 hybridization for the central methanide carbon atom.

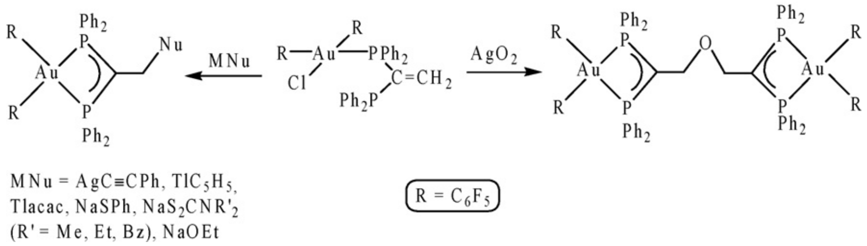
Similar cyclic methanide complexes with general formula $[Au(C_6F_5)_2\{(PPh_2)_2CCH_2Nu\}]$ [Nu = C≡CPh, C_5H_5, acac, SPh, S_2CNR_2 (R = Me, Et, Bz), OEt] or $[\{Au(C_6F_5)_2\{(PPh_2)_2CCH_2\}\}_2O]$, intermediates in Michael-type additions of HNu to the C=C bond of vdpp, are obtained by reaction of $[Au(C_6F_5)_2Cl\{PPh_2C(=CH_2)PPh_2\}]$ with C, S or O-donor nucleophiles (Scheme 24) [115] due to the strong activation of the carbon–carbon double bond of the diphosphine upon coordination with a gold(III) center.

The crystal structures of the thiophenol, diethyldithiocarbamate and oxide derivatives, established by X-ray diffraction methods [115], resemble those of the $(PPh_2)_3C^-$ species commented above, with distorted square-planar geometry at gold (phosphine bite angle 69.87(9), 69.97(6) and 69.9(3)°, respectively) and trigonal planar methanide carbon atoms. The negative charge of the methanide carbon is delocalized over the P–C bonds, giving them a degree of multiple bonding, while the C–C bond distance is consistent with a single bond.

Although non-cyclic gold methanides can be synthesized from $[Au(C_6F_5)_3(PPh_2CH_2PPh_2)]$, such as $NBu_4[\{Au(C_6F_5)_3(PPh_2CHPPh_2)\}_2Au]$ [117] or $[Au(C_6F_5)_3(PPh_2CHPPh_2)Au(tdppme)Mo(CO)_4]$ [122], by reaction with the appropriate acetylacetonategold(I) precursors, there are two main effective strategies for synthesizing them: the use of the phosphino-phosphonium or calcogenide

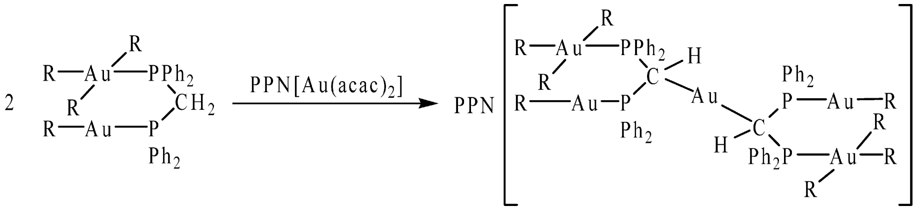


Scheme 23.



Scheme 24.

derivatives of dppm, where the formation of cycles is avoided because of the presence of the quaternary phosphorus; and the use of dinuclear complexes with a dppm bridging ligand, with a saturated coordination sphere for the metal centers, which also prevents ring formation. Thus, $[Au(C_6F_5)_3(PPh_2CH_2Ph_2P{=}E)]$ (E=O, S) or $[Au(C_6F_5)_nCl_x(PPh_2CH_2PPh_2Me)]ClO_4$ ($n = 1$, 3, $x = 0$; $n = 2$, $x = 1$) react with $[Au(acac)(PPh_3)]$ to afford $[Au(C_6F_5)_3\{PPh_2CH(AuPPh_3)Ph_2P{=}E\}]$ [85], $[Au(C_6F_5)\{PPh_2C(AuPPh_3)_2PPh_2Me\}]ClO_4$ or $[Au(C_6F_5)_nCl_{(3-n)}\{PPh_2CH(AuPPh_3)PPh_2Me\}]ClO_4$ ($n = 2$, 3) [126]. Thus, the two latter are obtained in a one-step reaction but can also be prepared in two stages, consisting in the deprotonation and coordination of the new gold fragment to the methanide carbon, as summarized in Scheme 25.

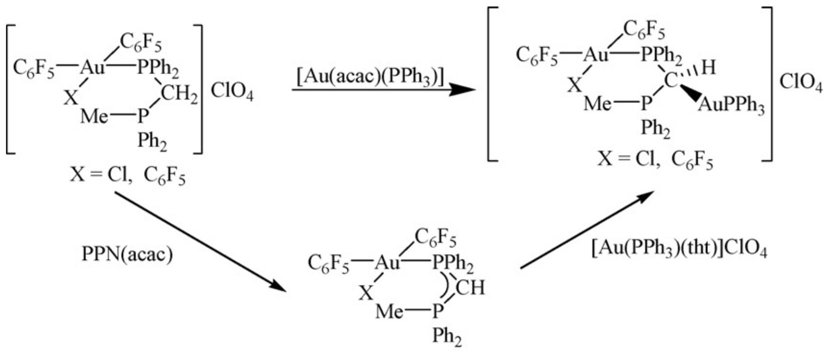


(16)

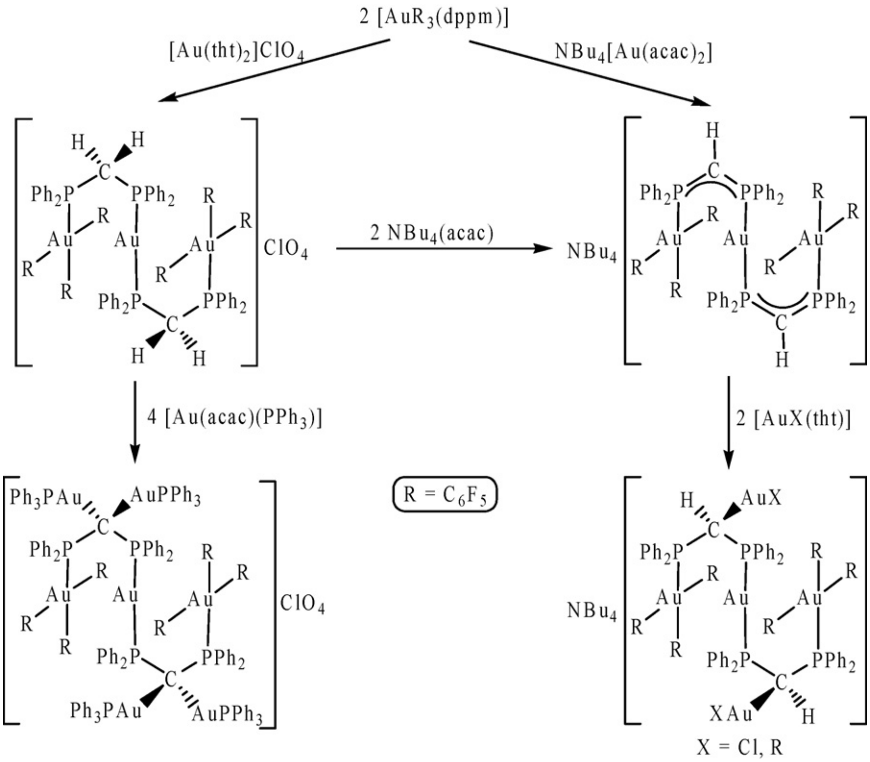
Similar reactions of $[Au(C_6F_5)_n(PPh_2CH_2PPh_2)Au(C_6F_5)]$ ($n = 1$, 3) with $[Au(acac)(PPh_3)]$ or with PPN(acac) followed by addition of $[Au(PPh_3)(tht)]ClO_4$ or $[AuX(tht)]$ enable the isolation of the di- or trinuclear species $[Au(C_6F_5)_n\{PPh_2CH(AuPPh_3)PPh_2\}Au(C_6F_5)]$ ($n = 1$, 3), $PPN[Au(C_6F_5)_3(PPh_2CHPPh_2)Au(C_6F_5)]$ or $PPN[Au(C_6F_5)_n\{PPh_2CH(AuX)PPh_2\}Au(C_6F_5)]$ (X = Cl, C_6F_5). The same strategy has been used to prepare higher nuclearity complexes, such as the pentanuclear anionic compounds $PPN[\{Au(C_6F_5)_3(PPh_2CHPPh_2)Au(C_6F_5)\}Au]$ [126] (Eq. (16)) or $NBu_4[\{Au(C_6F_5)_3\{PPh_2CH(AuX)PPh_2\}\}_2Au]$ [117] or the heptanuclear species $NBu_4[\{Au(C_6F_5)_3\{PPh_2C(AuPPh_3)_2PPh_2\}\}_2Au]$ [117] (Scheme 26).

The crystal structure of the trinuclear $NBu_4[\{Au(C_6F_5)_3(PPh_2CHPPh_2)\}_2Au]$ [117] displays similar features to those commented above, although no distortion of the square-planar or trigonal geometry at gold or methanide carbon, respectively, has been observed as the phosphino-methanide ligand acts as a bridge instead of as a chelate.

A special case is the formation of $[Au_4(C_6F_5)_2(PPh_2CHPPh_2)_2X_2]$ (X = Cl, Br) by oxidative addition of chlorine or bromine to the cyclic dimethanide $[Au_4(C_6F_5)_2(PPh_2CHPPh_2)_2]$ [127]. Displacement of chlorine by reaction with $[Ag(OClO_3)L]$ (L = tht, PPh_3, PPh_2Me, $PTol_3$) produces the cationic complexes $[Au_4(C_6F_5)_2(PPh_2CHPPh_2)_2L_2](ClO_4)_2$. The crystal structure



Scheme 25.



Scheme 26.

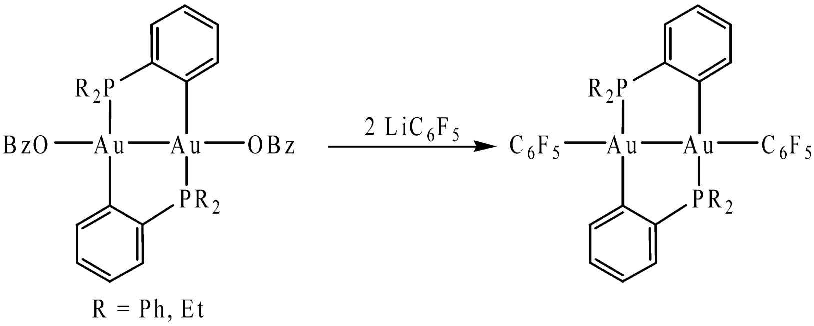
of the triphenylphosphine compound shows its backbone as a linear chain of three four-coordinated gold atoms in a distorted planar environment with Au–Au distances of 2.7305(11) Å (see Fig. 12) [127]. The formal charge of the Au_3 unit is +5, but integral oxidation states consistent with normal coordination geometry cannot be assigned. It is tentatively described as Au^{II}–Au^{I}–Au^{II}, but other possibilities cannot be ruled out.

4.2.2.5. Heterofunctional phosphines. The phosphino alkynyl derivative PPN[(C_6F_5)Au(μ-$PPh_2C{\equiv}C$)Au(C_6F_5)] has recently been prepared by treatment of [Au(C_6F_5)($PPh_2C{\equiv}CH$)] with sodium methoxide in the presence of chloropentafluorophenylgold(I) [104], as shown in Eq. (17).

$$[Au(C_6F_5)(PPh_2C{\equiv}CH)] \xrightarrow[+\ NaOMe/MeOH]{PPN[Au(C_6F_5)Cl]} PPN[(C_6F_5)Au(\mu\text{-}PPh_2C{\equiv}C)Au(C_6F_5)] \quad (17)$$

The use of acetylacetonate metal complexes as deprotonating agent has been also be employed for the synthesis of the related Au^{III} or mixed Au^{III}/M^{I} complexes [$(C_6F_5)_3$Au($PPh_2C{\equiv}C$)M(PPh_3)] (M = Au, Ag), [{$(C_6F_5)_3$Au(μ-$PPh_2C{\equiv}C$)Au}$_2$(μ-dppe)] or PPN[{$(C_6F_5)_3$Au (μ-$PPh_2C{\equiv}C$)}$_2$Au] from [Au$(C_6F_5)_3$($PPh_2C{\equiv}CH$)] (Scheme 27) [110].

Arylation with LiC_6F_5, a traditional method for synthesizing pentafluorophenylgold species, has recently yielded cycloaurated Au^{II} [Au(C_6F_5)(μ-2-$PR_2C_6H_4$)]$_2$ (R = Ph, Et) or mixed Au^{III}/Au^{I} [(C_6F_5)Au(μ-2-PPh_2-6-MeC_6H_3)Au(C_6F_5)(η^2-2-PPh_2-6-MeC_6H_3)] from their corresponding benzoate analogs, as shown in Eqs. (18) and (19) [116,128]. As commented above (see Eq. (15)), the digold(II) complex gives the zwitterionic heterovalent complexes [Au{μ-2,2′-($PR_2C_6H_4$)}$_2$Au$(C_6F_5)_2$] after prolonged heating in toluene as by-products in the synthesis of [{(C_6F_5)Au}$_2${μ-2,2′-($PR_2C_6H_4$)$_2$}] [116].



(18)

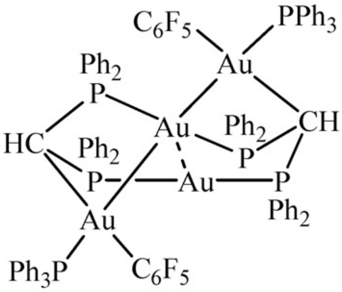
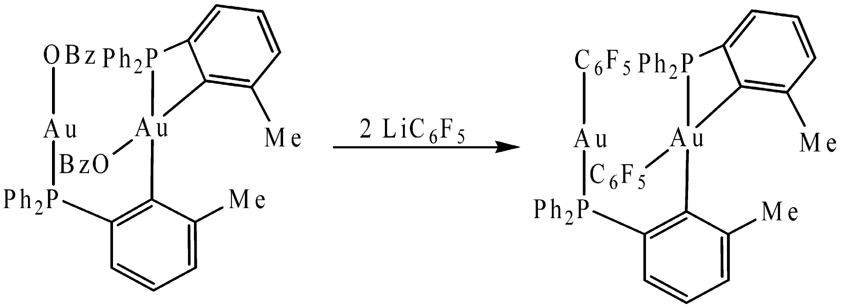


Fig. 12. Structure of the cation $[Au_4(C_6F_5)_2(PPh_2CHPPh_2)_2L_2]$

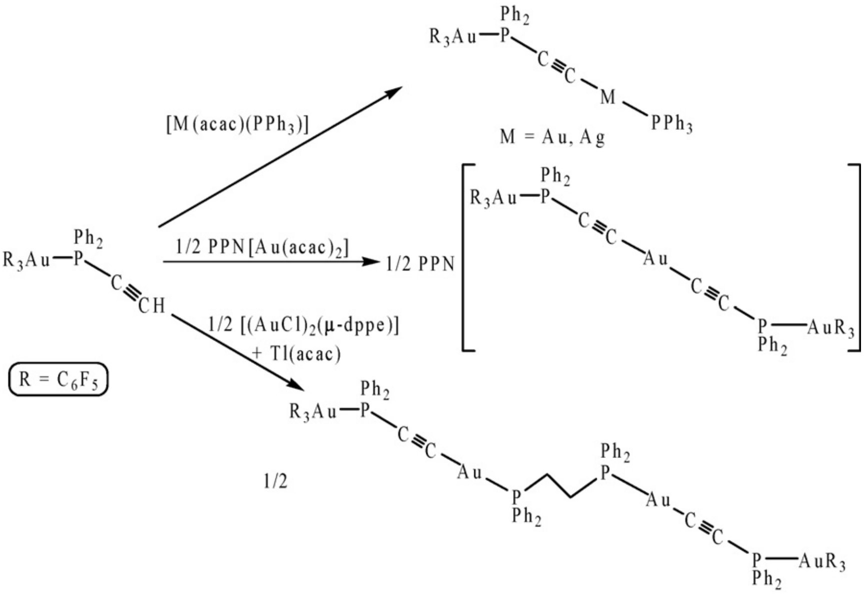


(19)

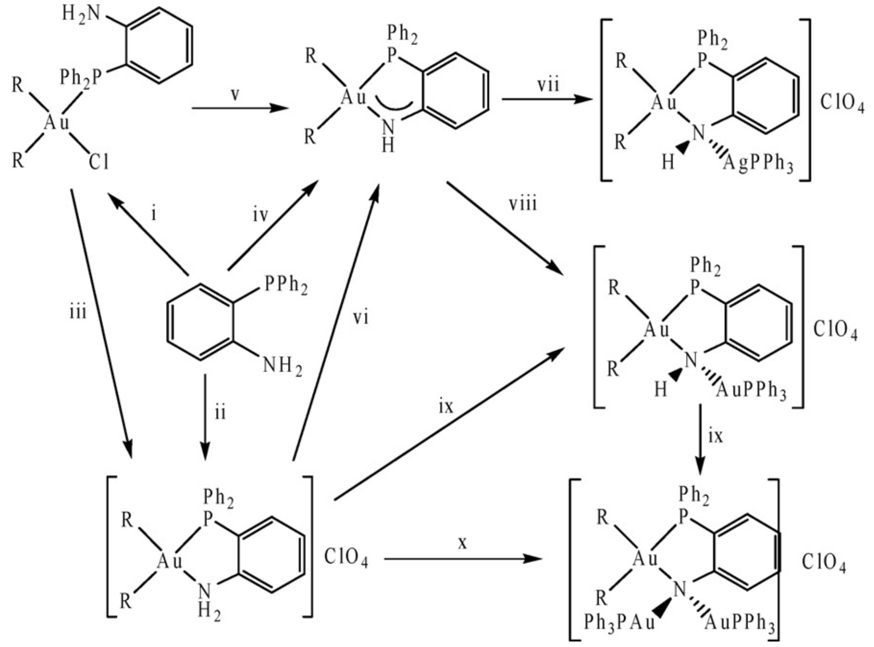
The Au–P and Au–C bond distances *trans* to P and *trans* to C in the crystal structures of some of these compounds reflect a similar *trans* influence for both types of ligands, and, as observed in other molecular structures commented in Sections 3.4 and 4.2.2.2, curiously the Au^{III}–P (2.374(1) and 2.3572(8) Å) and Au^{III}–C (2.063(8)–2.099(4) Å) lengths are longer than the Au^{I}–P (2.274(1)–2.309(5) Å) and Au^{I}–C (1.982(8) and 2.056(4) Å) ones [110,116,128]. The dinuclear $[Au(C_6F_5)(\mu\text{-}2\text{-}PPh_2C_6H_4)]_2$ [116] and $[(C_6F_5)Au(\mu\text{-}2\text{-}PPh_2\text{-}6\text{-}MeC_6H_3)Au(C_6F_5)(\eta^2\text{-}2\text{-}PPh_2\text{-}6\text{-}MeC_6H_3)]$ [128] display short intramolecular Au–Au distances of 2.6139(4) and 3.1948(2) Å, according to the presence of a metal–metal bond in the gold(II) complex and suggesting a weak interaction in the mixed-valence compound.

Regarding P, N-donor ligands, a series of phosphino-amine and -amido derivatives of 2-(diphenylphosphino)aniline $[2\text{-}PPh_2(C_6H_4NH_2), PNH_2]$ have been described [109]. The cationic $[Au(C_6F_5)_2\{\eta^2\text{-}PPh_2(2\text{-}C_6H_4NH_2)\}]ClO_4$ can be obtained from the free ligand or by elimination of chlorine from *cis*-$[Au(C_6F_5)_2Cl\{PPh_2(2\text{-}C_6H_4NH_2)\}]$, as shown in Scheme 28. Both mononuclear products, as well as uncoordinated 2-(diphenylphosphino)aniline, afford the phosphino-amido complex $[Au(C_6F_5)_2\{\eta^2\text{-}PPh_2(2\text{-}C_6H_4NH\}]$ when treated with the adequate acetylacetonate reagent, which then reacts with $[M(OClO_3)(PPh_3)]$ (M = Au, Ag) to give the dinuclear $[Au(C_6F_5)_2\{\eta^2\text{-}PPh_2\{2\text{-}C_6H_4NH(MPPh_3)\}\}]ClO_4$. The digold product can also be obtained by reaction of $[Au(C_6F_5)_2\{\eta^2\text{-}PPh_2(2\text{-}C_6H_4NH_2)\}]ClO_4$ with $[Au(acac)(PPh_3)]$ (1:1), and when the molar ratio is 1:2 the trinuclear species $[Au(C_6F_5)_2\{\eta^2\text{-}PPh_2\{2\text{-}C_6H_4N(AuPPh_3)_2\}\}]ClO_4$ is the resulting product (see Scheme 28).

The solid-state structures of $[Au(C_6F_5)_2\{\eta^2\text{-}PPh_2(2\text{-}C_6H_4NH_2)\}]ClO_4$, $[Au(C_6F_5)_2\{\eta^2\text{-}PPh_2(2\text{-}C_6H_4NH\}]$ and $[Au(C_6F_5)_2\{\eta^2\text{-}PPh_2\{2\text{-}C_6H_4N(AuPPh_3)_2\}\}]ClO_4$ show the



Scheme 27.



Scheme 28. R = C_6F_5; (i) 1/2 $[AuR2(\mu\text{-}Cl)]_2$; (ii) $[AuR_2(OEt_2)_2]ClO_4$; (iii) $AgClO_4$; (iv) $[Au(acac)R_2]$; (v) Tl(acac); (vi) PPN(acac); (vii) $[Ag(OClO_3)(PPh_3)]$; (viii) $[Au(OClO_3)(PPh_3)]$; (ix) $[Au(acac)(PPh_3)]$; (x) 2 $[Au(acac)(PPh_3)]$.

gold(III) centers in a square-planar environment bonded to two pentafluorophenyl rings and chelated by the PNH_2, $[PNH]^-$ or $PN(AuPPh_3)_2$ ligands [109]. The narrowest angle is always the one restricted by the chelating ligand (812.09(13)–84.81(16)°). The Au^{III}–C bond distances clearly indicate a higher *trans* influence of the PPh_2 group than the NH_2 or $N(AuPPh_3)_2$, as well as a higher *trans* influence from the deprotonated NH group than from NH_2 or $N(AuPPh_3)_2$ since the Au–C distances in $[Au(C_6F_5)_2\{\eta^2\text{-}PPh_2(2\text{-}C_6H_4NH)\}]$ are more similar. An intramolecular interaction between the gold(I) centers (2.9749(3) Å) is present in the trinuclear derivative (Fig. 13), and the Au^I–Au^{III} distances of 3.3219(3) and 3.4961(3) Å may indicate weak interactions between the gold(I) and the gold(III) centers, which, although infrequent, have also been described in other complexes and have been the object of theoretical studies [34,35,45,128].

The monooxidized dppmO in $[Au(C_6F_5)_3(PPh_2CH_2Ph_2P{=}O)]$ acts as P, O-donor ligand in the gold/thallium products $[\{Au(C_6F_5)_3(\mu\text{-}PPh_2CH_2Ph_2PO)\}_2Tl(C_6F_5)_2X]$ (X = Cl, C_6F_5) synthesized by reaction of the former with $[Tl(C_6F_5)_2Cl]$ or $[Tl(C_6F_5)_3(diox)]$ (diox = dioxane) [129]. The structure of the former (Fig. 14), determined by X-ray diffraction methods, shows similar Au–C and Au–P distances to other tris(pentafluorophenyl) phosphine

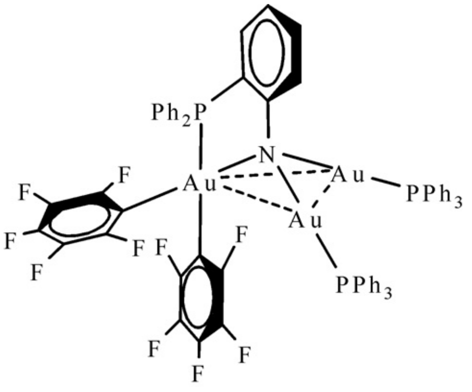
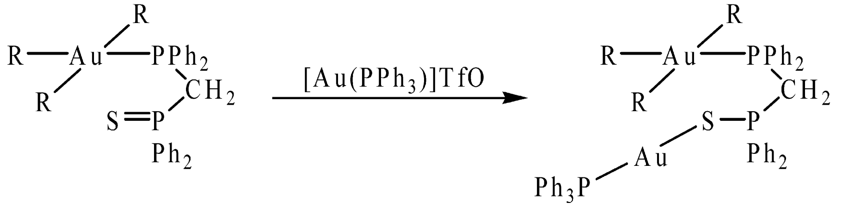


Fig. 13. Structure of $[Au(C_6F_5)_2\{PPh_2(2\text{-}C_6H_4N(AuPPh_3)_2]\}$

gold(III) complexes, indicating a nearly equal *trans* influence of the P- and C-donor ligands.

The sulfur atom of $[Au(C_6F_5)_3(PPh_2CH_2Ph_2P{=}S)]$ can also react with other metal complexes, such as $[Au(PPh_3)]TfO$, to give a species with the ligand acting as P, S-donor, namely $[Au(C_6F_5)_3(\mu\text{-}PPh_2CH_2Ph_2PS)Au(PPh_3)]$ [85] (Eq. (20)).



(20)

The same type of reaction prompts the synthesis of the snake-type complexes $[\{Au(C_6F_5)\}_2(\mu\text{-}PPh_2CH_2SPh)_2M]TfO$ (M = Cu, Ag) by addition of $[Cu(NCMe)_4]TfO$ or AgTfO to a solution of $[Au(C_6F_5)(PPh_2CH_2SPh)]$ (1:1 or 1:2) [106]

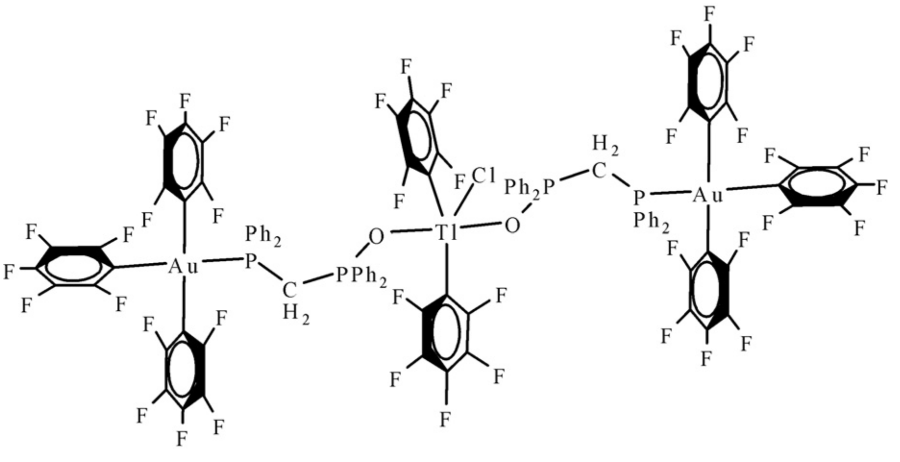


Fig. 14. Structure of $[\{Au(C_6F_5)_3(PPh_2CH_2Ph_2PO)\}_2Tl(C_6F_5)_2Cl]$

(Scheme 29). When the same reaction takes place using silver trifluoroacetate instead of triflate salt, the tetranuclear complex $[Au(C_6F_5)(\mu\text{-}PPh_2CH_2SPh)Ag(\mu\text{-}CF_3CO_2)]_2$ is isolated; this is an example of how changes in a counterion can significantly affect the final geometry of a product [106]. If the molar ratio of the reagents in this reaction is 2:1 instead of 1:1, a complex of stoichiometry $[AuAg_2(C_6F_5)(CF_3CO_2)_2(PPh_2CH_2SPh)]$, in which the thioether ligand is expected to be coordinated to two silver trifluoroacetate moieties through the silver atoms, is obtained.

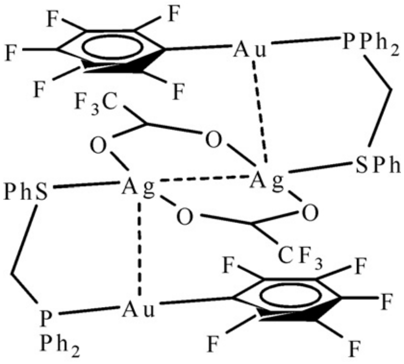
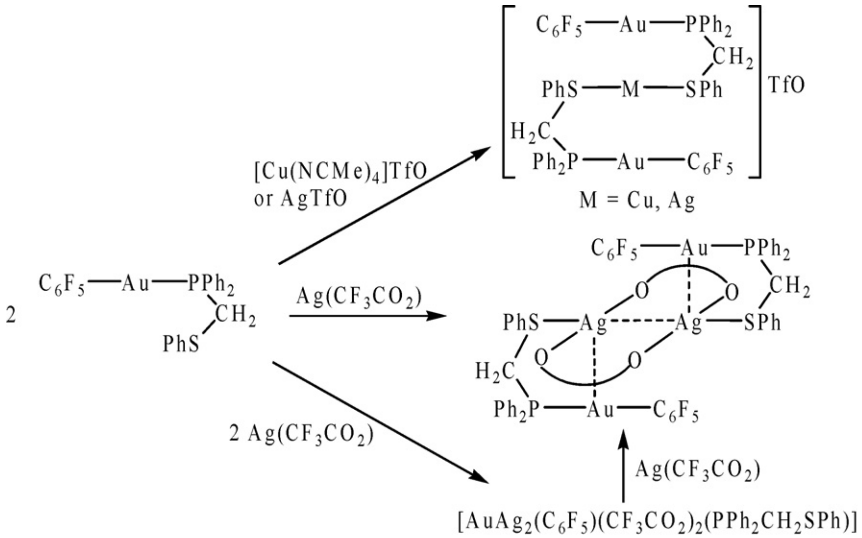
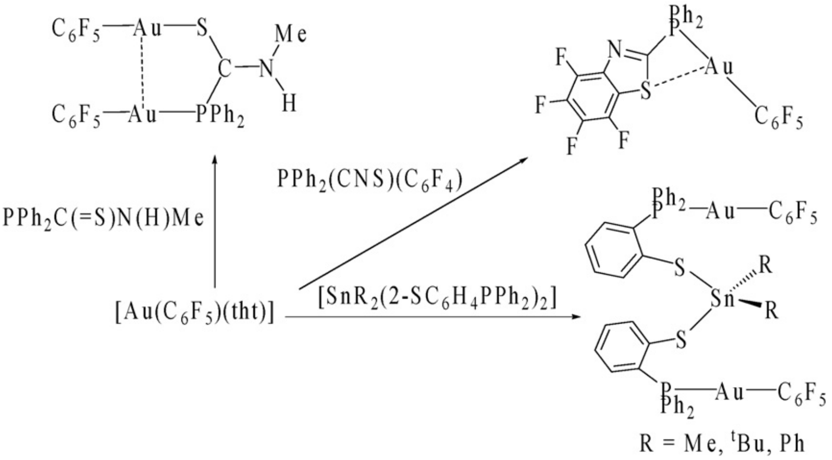


Fig. 15. Structure of $[Au(C_6F_5)(PPh_2CH_2SPh)Ag(CF_3CO_2)]_2$

The crystal structure of the Au_2Ag_2 species (Fig. 15) shows the metallic centers forming a zig-zag chain with the Ph_2PCH_2SPh ligands bridging the gold and silver atoms (with Au–P and Ag–S bonds) and the silver atoms bridged by the trifluoroacetate ligands. There are short Au···Au and Ag···Ag bonding interactions of 3.0335(8) and 2.8155(9) Å. The former is slightly longer than in the related $[AuAg(\mu\text{-}PPh_2CH_2SPh)_2](TfO)_2$ (2.9314(5) Å) [106], whereas the latter is shorter than in the homodinuclear $[Ag(\mu\text{-}PPh_2CH_2SPh)]_2(ClO_4)_2$ (2.9732(9) Å) [130] and even shorter than the values found in metallic silver (2.89 Å) or in many silver oxides [131]. The geometry at the gold centers is distorted from the linearity (C–Au–P 170.16(9)°), perhaps as a consequence of the Au···Ag interaction, while the silver atoms present a more irregular geometry.



Scheme 29.



Scheme 30.

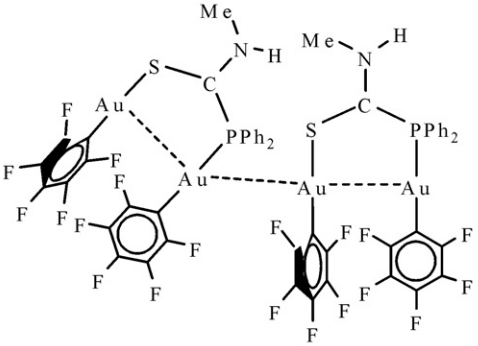


Fig. 16. Structure of $[\{Au(C_6F_5)\}_2\{PPh_2C(=S)N(H)Me\}$

Again, the use of $[Au(C_6F_5)(tht)]$ has been shown as a useful pathway for the synthesis of new arylgold(I) compounds. Thus, its treatment with free P, S-donor ligands, such as diphenylphosphinothioformamide $[PPh_2C(=S)N(H)Me]$ or the perfluorinated benzothiazolephosphine ligand $PPh_2(CNS)(C_6F_4)$, or with metal complexes with donor capacity, such as $[SnR_2(2\text{-}SC_6H_4PPh_2)_2]$ (R = Me, ^{t}Bu, Ph), afford the neutral species $[\{Au(C_6F_5)\}_2\{\mu\text{-}PPh_2C(=S)N(H)Me\}]$ [105], $[Au(C_6F_5)\{\mu\text{-}PPh_2(CNS)(C_6F_4)\}]$ [132] or the Sn^{IV}/Au^{I} derivatives $[\{Au(C_6F_5)(2\text{-}PPh_2C_6H_4S)\}_2SnR_2]$ [133] (Scheme 30).

In the case of $[\{Au(C_6F_5)\}_2\{\mu\text{-}PPh_2C(=S)N(H)Me\}]$ [105], although it is considered a dinuclear compound, it crystallizes into tetranuclear units formed by an intermolecular Au···Au interaction of 3.2712(5) Å between two dinuclear units (Fig. 16) and it is described in the paper as a tetranuclear complex. The shortest intermetallic distances between adjacent tetranuclear units of approximately 6 Å. The intermolecular Au···Au contact is longer than the intramolecular distances, which are 3.1631(5) and 3.0391(5) Å. These intramolecular distances are associated with the *cis* conformation observed in the complex, which is also the preferred conformation in dinuclear products containing a single dppm bridge, such as $[\{Au(C_6H_5)\}_2(\mu\text{-dppm})]$ (3.154(1) Å) [134] or $[\{Au(C_6F_5)\}_2(\mu\text{-dppm})]$ (3.162(1) Å) [135] or in the biphenyl derivative $[\{Au(C_6F_5)\}_2\{\mu\text{-}2,2'\text{-}(PPh_2C_6H_4)_2\}]$ (3.0688(8) Å) [116].

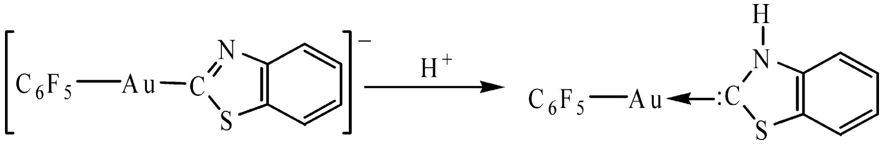
$[Au(C_6F_5)\{\mu\text{-}PPh_2(CNS)(C_6F_4)\}]$ has been included in this section although the sulfur atom of $PPh_2(CNS)(C_6F_4)$ only there is only weak interaction with the gold centers (Au–S distance 3.3409(9) Å) [132]. The crystal structure of $[\{Au(C_6F_5)(2\text{-}PPh_2C_6H_4S)\}_2Sn^tBu_2]$ [133] shows no significant interactions between the metallic centers.

Finally, the comparison of Au^{I}–P distances *trans* to phosphorus (2.269(3)–2.2886(10) Å) and *trans* to nitrogen (2.2395(9)–2.2505(9) Å) in the species containing heterofunctional phosphines that have been structurally characterized reconfirms the higher *trans* influence of the P-donor ligands when compared with P-donor ones. Similarly, the comparison of the Au^{III}–C bond lengths *trans* to phosphorus (2.050(5)–2.088(8) Å), C_6F_5 (2.063(8)–2.099(4) Å) and nitrogen (2.019(6)–2.053(4) Å) indicate that the *trans* influence produced by the C-donor and P-donor ligands is of the same order and stronger than that from N-donor ligands.

5. Group 14 donor atom ligands

5.1. Carbenes and carbines

A small number of carbene and carbine gold complexes have been described in recent years, such as the monocarbene $[Au(C_6F_5)(\overline{CNHC_6H_4S}\text{-}o)]$ [136] $[Au(C_6F_5)\{\overline{CN(Me)C(Me)=CHS}\}]$ [136] or $[Au(C_6F_5)\{\overline{CCH=CHN(Me)S}\}]$ [137], obtained by protonation or methylation from their corresponding thiazolyl or isothioazolyl derivatives, as exemplified for the former in Eq. (21).



(21)

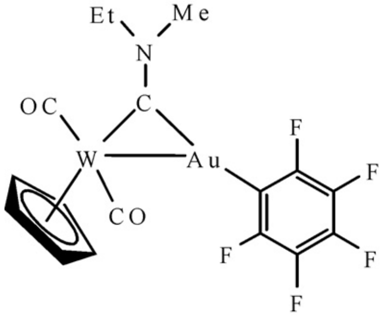
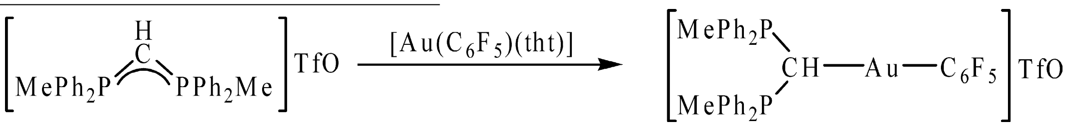


Fig. 17. Structure of $[Au(C_6F_5)\{CN(Et)Me\}W(C_5H_5)(CO)_2]$

The displacement reaction of $[W\{(CN(Et)Me\}(\eta^5\text{-}C_5H_5)(CO)_2]$ with $[Au(C_6F_5)(tht)]$ has enabled the synthesis of the hetero-nuclear aminocarbyne $[Au(C_6F_5)\{\mu\text{-}CN(Et)Me\}W(\eta^5\text{-}C_5H_5)(CO)_2]$ [138], an adduct that exhibits a molecule of the starting product bonded to the $Au(C_6F_5)$ fragment through one of the $W\text{–}C_{carbyne}$ π bonds, with the formation of a WCAu ring (see Fig. 17). The tungsten atom acquires its closed electronic configuration through a mechanism which is somewhere in between the resonance structures $N\text{–}C{\equiv}W$ and $N^+{=}C{=}W^-$. The $Au(C_6F_5)$ fragment achieves the preferred two-coordinative 14-electron configuration by accepting an electron pair from the in-plane localized $W\text{–}C_{carbyne}$ π orbital, resembling the coordination of an olefin ligand. This interaction perturbs, but does not disrupt, the electronic structure of the donor.



$$[CH(PPh_2Me)_2]TfO \xrightarrow{[Au(C_6F_5)(tht)]} [Au(C_6F_5)\{CH(PPh_2Me)_2\}]TfO \quad (22)$$

The Au–W and $Au\text{–}C_{carbyne}$ distances of 2.727(1) and 2.13(2) Å, respectively, can be compared with the corresponding values in the related compound $[AuWBr(bipy)(C_6F_5)(CO)_2(\mu\text{-}CC_6H_4Me\text{-}4)]$ (2.783(1) and 2.080(3) Å) [139] and the $Au\text{–}C_{aryl}$ distance of 2.07(2) Å compares well with that observed in $[Au(Fmes)(Me_3SiC{\equiv}C)_2Ti(\eta^5\text{-}C_5H_4SiMe_3)_2]$ (2.079(7) Å) [140,141].

5.2. Alkynyls

Alkynylgold compounds are poorly represented, and only the ethynylgold(I) derivative $PPN[Au(C_6F_5)(C{\equiv}CH)]$ has been described in recent years, and which is obtained from treatment of $PPN[Au(C_6F_5)(acac)]$ with C_2H_2 [142].

Its crystal structure (Fig. 18) displays a quasi-linear $C\text{–}Au\text{–}C{\equiv}CH$ fragment with C–Au–C and $Au\text{–}C{\equiv}C$ bond angles of 176.9(2) and 174.6(5)°, respectively. The $Au\text{–}C_{aryl}$ bond distance in this complex (2.049(5) Å), as well as that in the related $PPN[Au\{2,4,6\text{-}(NO_2)_3C_6H_2\}(C{\equiv}CH)]$ [142] (2.039(5) Å), are longer than the $Au\text{–}C_{ethynyl}$ lengths of 1.984(6) and 2.0148(56) Å, respectively, consistent with a stronger *trans* influence of alkynyl than aryl ligands.

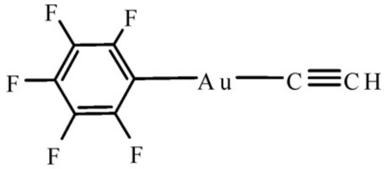


Fig. 18. Structure of the cation $Au(C_6F_5)(CCH)]$

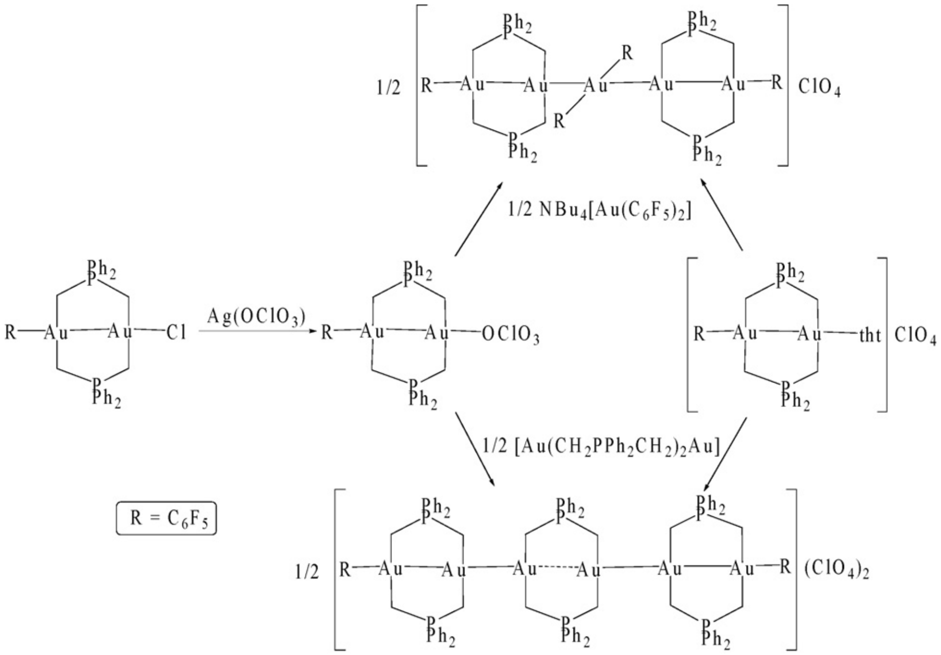
5.3. Ylides

Although the chemistry of gold ylides was extensively developed in the eighties and led to the description of many gold(II) species, this field of research has been less productive in recent years, with only a few gold ylides having been reported in this period. The phosphoranium salt $[CH(PPh_2Me)_2]TfO$, synthesized from the ylide $[PPh_2CH{=}PPh_2Me]$, reacts with $[Au(C_6F_5)(tht)]$ to afford its first metallic complex, $[Au(C_6F_5)\{CH(PPh_2Me)_2\}]TfO$, which, despite the weak nucleophilic character of the ylidic carbon, is stable [143] (Eq. (22)).

Its crystal structure displays a $Au\text{–}C_{aryl}$ distance of 2.029(6) Å, of the same order as those found in related complexes with C_6F_5 groups *trans* to an ylidic carbon atom (mean distance 2.024 Å) [144–146] and close to the $Au\text{–}C_{aryl}$ distance in $PPN[Au(C_6F_5)(C{\equiv}CH)]$ (2.049(5) Å), commented above [142]. The $Au\text{–}C_{ylide}$ bond length (2.112(6) Å) is longer than the $Au\text{–}C_{aryl}$ one, and its value agrees well with those in the complexes mentioned and with a stronger *trans* influence from the aryl group than from ylide ligands.

Reaction of the asymmetric gold(II) ylide $[(C_6F_5)Au(CH_2PPh_2CH_2)_2AuCl]$ with silver perchlorate led to $[(C_6F_5)Au(CH_2PPh_2CH_2)_2Au(OClO_3)]$ [147], which further reacts with gold(I) species such as $NBu_4[Au(C_6F_5)_2]$ or $[Au(CH_2PPh_2CH_2)_2Au]$ in a 2:1 molar ratio (Scheme 31) to give the penta- or hexanuclear derivatives $[\{(C_6F_5)Au(CH_2PPh_2CH_2)_2Au\}_2Au(C_6F_5)_2]ClO_4$ or $[\{(C_6F_5)Au(CH_2PPh_2CH_2)_2Au\}_2Au(CH_2PPh_2CH_2)_2Au]\text{-}(ClO_4)_2$, respectively. The same results can be achieved if the reactions are carried out with $[(C_6F_5)Au\text{-}(CH_2PPh_2CH_2)_2Au(tht)]$.

Although none of them have been structurally characterized, the molecular structure of the hexanuclear 2,4,6-trifluorophenyl derivative was determined by X-ray diffraction methods, showing an hexametallic $Au^{II}\text{–}Au^{II}\text{–}Au^{I}\cdots Au^{I}\text{–}Au^{II}\text{–}Au^{II}$ skeleton comprising three pairs of gold atoms, each doubly bridged by two bis-ylide ligands, and the three $[Au(CH_2PPh_2CH_2)_2Au]$ moieties held together through two unsupported Au–Au bonds of 2.7370(7) Å [147].



Scheme 31.

6. Metal-containing ligands

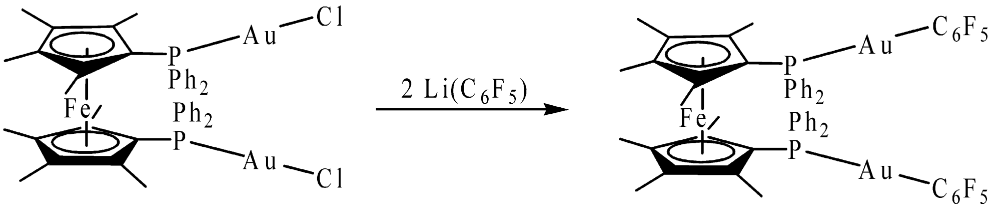
6.1. Ferrocene derivatives as ligands

The search of non-traditional ligands, and recent interest in the preparation of ferrocene-containing complexes due to their increasing role in the rapidly growing areas of organic synthesis and catalysis in material science [148–150], has led to the synthesis of a large number of functionalized ferrocene derivatives as ligands in recent years. Ferrocene has become a versatile building block for the synthesis of compounds with tailor-made properties, and numerous products in which one or both cyclopentadienyl rings are bound to organic groups containing one or more donor atoms have been reported [148].

For the isolation of perfluorophenylgold derivatives ligands with different donor atoms, such as sulfur [$Fc(S_2CNEt_2)_2$, $Fc(SPh)_2$, $Fc(PPh_2S)_2$], selenium [$Fc(SePh)_2$], nitrogen [Fcpy, $Fc(Spy)_2$, $FcCH_2pz$, $FcCH_2NHpyMe$, Fcterpy] or phosphorus [$FcCH_2PPh_2$, $FcCH_2PPh_2CH_2PPh_2^+$, $Fc(SPh)PPh_2$, $Fc(SePh)PPh_2$, PFc_2Ph, $Fc'(PPh_2)_2$], [Fc = ferrocenyl $(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$ or ferrocenediyl, $Fe(\eta^5\text{-}C_5H_4)_2$; Fc′ = octamethylferrocenediyl, $Fe(\eta^5\text{-}C_5Me_4)_2$] have been employed.

The donor atoms present in these ligands have enough donor capability to displace weakly coordinated molecules, such as tetrahydrothiophene or diethyl ether, from their gold(I) or gold (III) complexes, or to break the chlorine bridges in $[Au(C_6F_5)_2(\mu\text{-}Cl)]_2$, affording different nuclearity heterometal Au/Fe products of the types $[Au(C_6F_5)L]$, $[\{Au(C_6F_5)\}_2L]$, $[\{Au(C_6F_5)\}_3L]$, $[Au(C_6F_5)_3L]$, $[Au(C_6F_5)_2ClL]$, $[Au(C_6F_5)_2L]ClO_4$, $[Au(C_6F_5)_2L_2]ClO_4$, $[\{Au(C_6F_5)_3\}_2L]$ or $[\{Au(C_6F_5)_2Cl\}_2L]$, which are summarized in Tables 1 and 2 [151–163].

Different synthetic procedures can only be followed in specific cases, for example in the case of the 1,1′-bis(diphenylphosphino)octamethylferrocene derivative $[\{Au(C_6F_5)\}_2\{Fc'(PPh_2)_2\}]$, a complex that can be alternatively obtained by arylation of the chlorine derivative with $Li(C_6F_5)$ [158] (Eq. (23)). This species, as well as other related Au/Fe complexes containing the same ligand, has been tested *in vitro* against various human cancer cells. Cytotoxicity, although improved by the presence of gold, is not better than that of known drugs. Its related mononuclear compound $[\{\mu\text{-}Au(C_6F_5)\}\{Fc'(PPh_2)_2\}]$ was the first example of a P–Au(–P)–C tricoordinate gold(I) [158].



(23)

Table 1
Gold(I) complexes with ferrocene derivatives as ligands

Complex	Au–C (Å)	Au–N (Å)	Au–P (Å)	Au···Au (Å)	Reference
[Au(C$_6$F$_5$)(Fcpy)]	2.00(2)	2.124(15)		3.301(2)	151
[Au(C$_6$F$_5$)(FcCH$_2$pz)]	2.023(7)	2.072(5)		3.1204(6)	152
[Au(C$_6$F$_5$)(FcCH$_2$NHpyMe)]	1.988(4)	2.073(4)		3.429	153
[Au(C$_6$F$_5$)(FcCH$_2$PPh$_2$)]	2.070(5)		2.284(2)	[5.560]	154
[Au(C$_6$F$_5$){Fc(SPh)PPh$_2$}]	2.056(6)		2.2701(16)		155
[Au(C$_6$F$_5$){Fc(SePh)PPh$_2$}]	2.049(5) 2.037(5)		2.2773(14) 2.2643(15)		155
[Au(C$_6$F$_5$)(FcCH$_2$PPh$_2$CH$_2$PPh$_2$)]TfO					156
[Au(C$_6$F$_5$)(PFc$_2$Ph)]					157
[{μ-Au(C$_6$F$_5$)}{Fc′(PPh$_2$)$_2$}]					158
[{Au(C$_6$F$_5$)}$_2${Fc(Spy)$_2$}]					159
[{Au(C$_6$F$_5$)}$_2${Fc(PPh$_2$S)$_2$}]					160
[{Au(C$_6$F$_5$)}$_2${Fc′(PPh$_2$)$_2$}]					158
[{Au(C$_6$F$_5$)}$_3$(η^3-Fcterpy)]		2.068(10)–2.106(8)		3.0678(6)–3.1559(7)	161
[Au(C$_6$F$_5$){FcCH$_2$N(AuPPh$_3$)pyMe}]					153

The heterotrinuclear product [Au(C$_6$F$_5$){FcCH$_2$N(AuPPh$_3$)pyMe}], which contains a mixed pyridine–amide ligand, is obtained in good yield by deprotonation of the NH group of the ferrocene ligand 6-[(ferrrocenylmethyl)amino]-2-picoline present in [Au(C$_6$F$_5$){FcCH$_2$NHpyMe}] with [Au(acac)(PPh$_3$)] and simultaneous coordination of AuPPh$_3$$^+$ moiety [153] (Eq. (24)).

Table 2
Gold(III) complexes with ferrocene derivatives as ligands

Complex	Au–C (Å)	Au–N (Å)	Au–S (Å)	Au–P (Å)	Reference
[Au(C$_6$F$_5$)$_3$(Fcpy)]	$2.017(3)_{\mathrm{N}}$ $2.067(3)_{\mathrm{R}}$ $2.068(3)_{\mathrm{R}}$	2.101(3)			151
[Au(C$_6$F$_5$)$_3$(FcCH$_2$pz)]					152
[Au(C$_6$F$_5$)$_3$(FcCH$_2$NHpyMe)]	$2.026(6)_{\mathrm{N}}$ $2.064(5)_{\mathrm{R}}$ $2.071(5)_{\mathrm{R}}$	2.104(4)			153
[Au(C$_6$F$_5$)$_3$(FcCH$_2$PPh$_2$)]	$2.067(3)_{\mathrm{P}}$ $2.080(4)_{\mathrm{R}}$ $2.068(4)_{\mathrm{R}}$			2.3503(9)	154
[Au(C$_6$F$_5$)$_3${Fc(SPh)PPh$_2$}]					155
[Au(C$_6$F$_5$)$_3${Fc(SePh)PPh$_2$}]					155
[Au(C$_6$F$_5$)$_3$(PFc$_2$Ph)]					157
[Au(C$_6$F$_5$)$_2$Cl(FcCH$_2$NHpyMe)]	$2.012(2)_{\mathrm{N}}$ $2.028(3)_{\mathrm{Cl}}$	2.101(2)			153
[Au(C$_6$F$_5$)$_2$Cl(PFc$_2$Ph)]					157
[Au(C$_6$F$_5$)$_2${Fc(SePh)PPh$_2$}]ClO$_4$					155
[Au(C$_6$F$_5$)$_2$(Fcpy)$_2$]ClO$_4$	$2.011(9)_{\mathrm{N}}$ $2.015(9)_{\mathrm{N}}$	2.076(7) 2.089(7)			151
[{Au(C$_6$F$_5$)$_3$}$_2${Fc(S$_2$CNEt$_2$)$_2$}]					162
[{Au(C$_6$F$_5$)$_3$}$_2${Fc(SPh)$_2$}]	$2.028(4)_{\mathrm{S}}$ $2.068(4)_{\mathrm{R}}$ $2.073(4)_{\mathrm{R}}$		2.3786(11)		163
[{Au(C$_6$F$_5$)$_3$}$_2${Fc(SePh)$_2$}]					163
[{Au(C$_6$F$_5$)$_3$}$_2${Fc(PPh$_2$S)$_2$}]					160
[{Au(C$_6$F$_5$)$_3$}$_2${Fc(Spy)$_2$}]	$2.005(5)_{\mathrm{N}}$ $2.058(6)_{\mathrm{R}}$ $2.077(6)_{\mathrm{R}}$	2.105(4)			159
[{Au(C$_6$F$_5$)$_3$}$_2${Fc(SePh)PPh$_2$}]					155
[{Au(C$_6$F$_5$)$_2$Cl}$_2${Fc(S$_2$CNEt$_2$)$_2$}]					162
[{Au(C$_6$F$_5$)$_2$Cl}$_2${Fc(PPh$_2$S)$_2$}]	$2.008(8)_{\mathrm{Cl}}$ $2.040(8)_{\mathrm{S}}$		2.386(2)		160

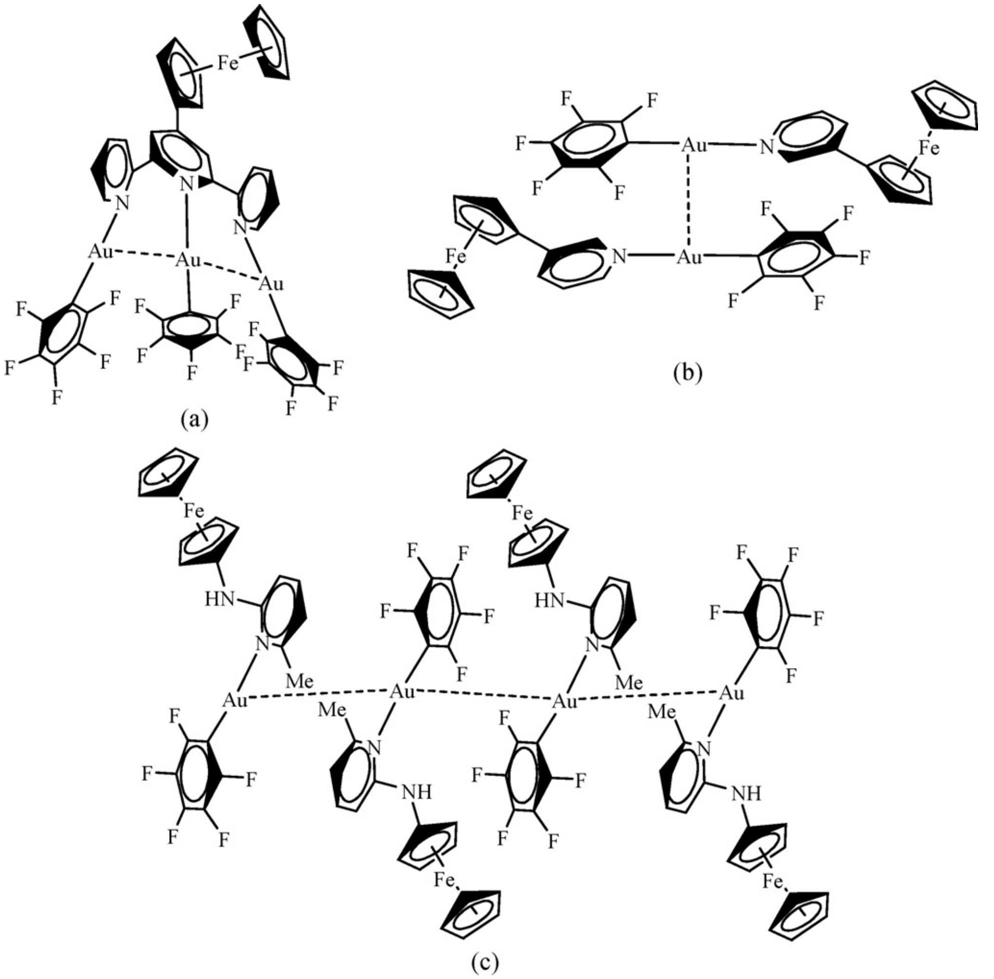
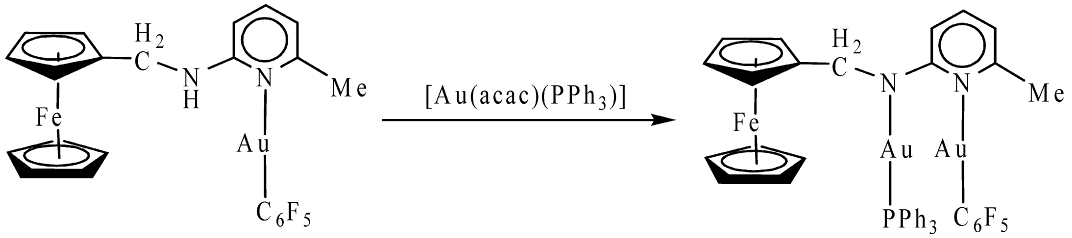


Fig. 19. Different Au—Au interactions is some ferrocenyl derivatives



(24)

The crystal structures of half the Au^I/Fe^{II} complexes have been determined by X-ray diffraction methods, showing a typical linear environment for the gold(I) center, nearly eclipsed aromatic rings at iron, and none of them display intramolecular Au···Fe interactions. $[Au(C_6F_5)(FcCH_2PPh_2)]$ [154], $[Au(C_6F_5)\{Fc(EPh)PPh_2\}]$ (E = S, Se) [155] and $[\{Au(C_6F_5)\}_3(\eta^3\text{-Fcterpy})]$ [161] do not display Au···Au interactions either (the shortest gold–gold distance in the former is 5.560 Å), but there are intramolecular Au···Au interactions of 3.0678(6) and 3.1559(7) Å in the terpy derivative that may contribute to the overall stability of the system (Fig. 19a), as was shown by DTF calculations [161], and intermolecular aurophilic contacts (see Table 1) that led to association into pairs in $[Au(C_6F_5)(Fcpy)]$ [151] (Fig. 19b) and $[Au(C_6F_5)(FcCH_2pz)]$ [152] or into chains in the case of $[Au(C_6F_5)(FcCH_2NHpyMe)]$ [153] (Fig. 19c). In the selenium derivative $[Au(C_6F_5)\{Fc(SePh)PPh_2\}]$, there is one intermolecular Au···Se contact of 3.643 Å that leads to the formation of couples as shown in Fig. 20 [155]. Furthermore, in most of the structures of gold(I) complexes, the lattice shows F···H and/or Au···H contacts that give rise to three-dimensional networks.

The gold(III) products that have been structurally characterized do not display intermolecular secondary interactions, aurophilic contacts or hydrogen bonds, and appear as monomers in the lattice with the exception of the 6-[(ferrocenylmethyl)amino]-2-picoline derivatives $[Au(C_6F_5)_2X(FcCH_2NHpyMe)]$ (X = Cl, C_6F_5) [153]. In these two species, apart from intramolecular N–H···Au and N–H···X hydrogen bonds, intermolecular C–H···F and C–H···Cl con-

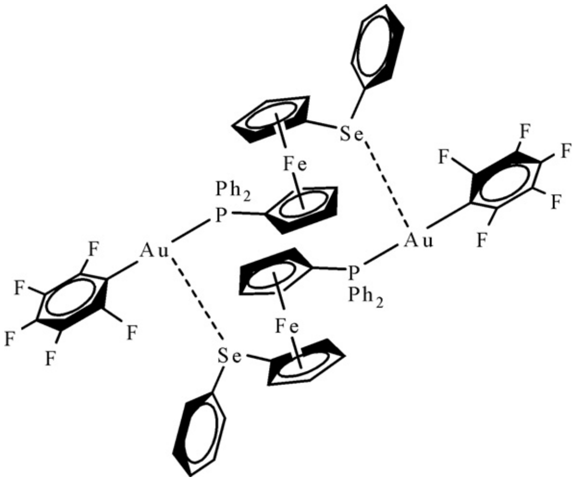


Fig. 20. Dimers pf $[Au(C_6F_5)\{Fc(SePh)PPh_2\}]$

tacts create a 3D structure in the former or lead to the disposition of the molecules into planes in the latter. Different intramolecular secondary interactions, such as C–H···O between the cation and the anion of $[Au(C_6F_5)_2(Fcpy)_2]ClO_4$ [151], C–H···Cl and C–H···F in $[\{Au(C_6F_5)_2Cl\}_2\{Fc(PPh_2S)_2\}]$ [160] or Au···Se in $[\{Au(C_6F_5)_3\}_2\{Fc(Spy)_2\}]$ [159], are present in other compounds. Although the sulfur atom is 3.124 Å from the gold(III) center in the 1,1′-bis(2-pyridylthio)ferrocene derivative, the position should be attributed more to the rigidity of the ligand than to any significant bonding interaction.

6.2. *Metalloligands*

6.2.1. *Au/Ag and Au/Cu complexes*

The use of bis(perhalophenyl)aurate(I) as Lewis base in order to generate unsupported Au···M interactions between closed-shell metal atoms by acid–base reactions with acid metal ions has increased continually in recent years. A number of polymeric Au^I/Ag^I complexes of stoichiometry $[Au_2Ag_2(C_6F_5)_4L_2]_n$ were prepared about 20 years ago using this strategy, as shown in Eq. (25) [164,165].

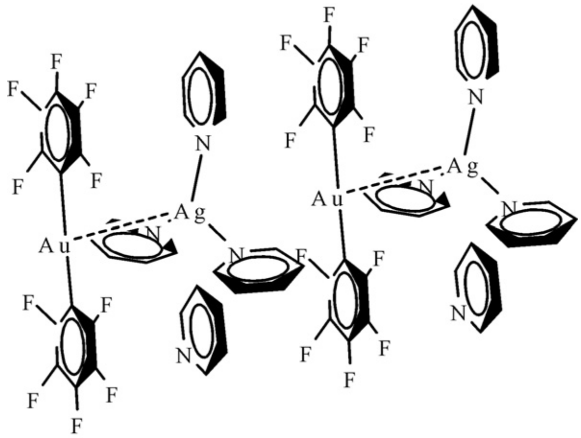


Fig. 21. Chains of $[AuAg(C_6F_5)_2(py)_4]$

Although they were isolated as solids whose colors varied from pale yellow to red, while in solution they were colorless. The optical properties of such materials were not studied until 2000, when $[Au_2Ag_2(C_6F_5)_4(O{=}CMe_2)_2]_n$ and its optical properties were studied in solid state at room temperature and at 77K, as well as in acetone solution. This yielded very interesting results [166]. The interesting properties and potential application of certain derivatives of this type as sensors based on vapochromic behavior has promoted the synthesis of new related species through similar procedures (see Table 3).

When the reaction shown in Eq. (25) is carried out in dichloromethane in the presence of excess pyridine, a colorless solid of stoichiometry $[AuAg(C_6F_5)_2(py)_4]$ is obtained [167]. The single-crystal X-ray diffraction study of this species shows the silver atom distorted over two positions (50% each one), which does not enable a valid analysis of its bond distances and angles. Anyway, it univocally shows an extended unsupported one-dimensional chain of alternating gold and silver atoms of the $[Ag(py)_3]^+$ and $[Au(C_6F_5)_2]^-$ units with the fourth pyridine molecule not coordinated to the metal centers (Fig. 21). This arrangement is the result of the formation of molecular Au–Ag ion pairs, to the π-stacking interactions between C_6F_5

$$NBu_4[Au(C_6F_5)_2] \xrightarrow{AgClO_4} [AuAg(C_6F_5)_2] \xrightarrow{n\ L} 1/2n\ [Au_2Ag_2(C_6F_5)_4L_2]_n \qquad (25)$$

Table 3
Gold/silver and gold/copper complexes

Complex	Au–C (Å)	C–Au–C (Å)	M···M (Å)	Au···M (Å)	Reference
$[AuAg(C_6F_5)_2(py)_4]_n$					[167]
$[Au_2Ag_2(C_6F_5)_4(1,10\text{-phen})_2]_n$					[168]
$[Au_2Ag_2(C_6F_5)_4(2,2'\text{-bipy})_2]_n$					[168]
$[Au_2Ag_2(C_6F_5)_4(tht)_2]_n$					[168]
$[Au_2Ag_2(C_6F_5)_4(O{=}CMe_2)_2]_n$	2.086(8)	177.3(3)	$3.1674(11)_{Au}$	2.7829(9)	[166]
	2.092(7)		$3.1810(13)_{Ag}$	2.7903(9)	
$[Au_2Ag_2(C_6F_5)_4(N{\equiv}CMe)_2]_n$	2.055(6)	175.9(2)	$2.8807(4)_{Au}$	2.7577(5)	[169]
	2.088(6)		$3.1084(10)_{Ag}$	2.7267(5)	
$[Au_2Cu_2(C_6F_5)_4(N{\equiv}CMe)_2]_n$	2.043(5)	175.92(15)	$2.9129(3)_{Au}$	2.5876(5)	[169]
	2.090(4)		$3.0197(11)_{Cu}$	2.5741(6)	
$[AuCu(C_6F_5)_2(N{\equiv}CMe)(N_2C_4H_4)]_n$	2.056(5)	178.09(16)		2.8216(6)	[170]
	2.045(5)				

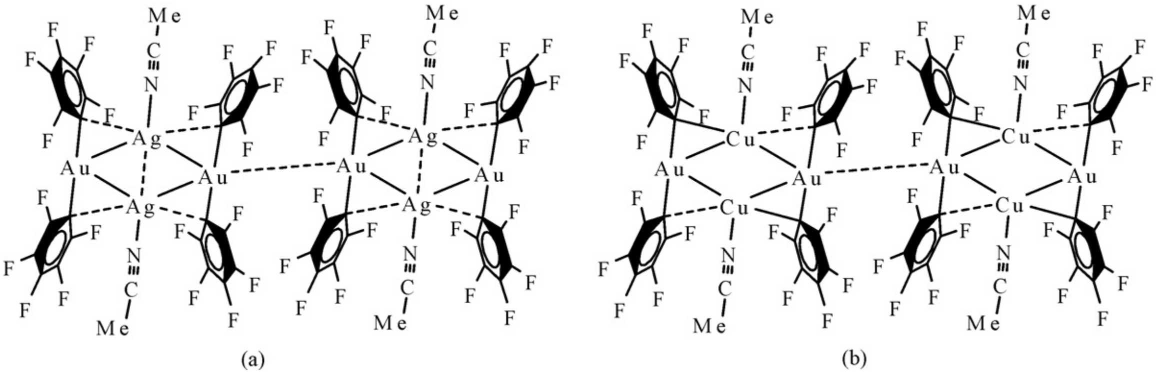


Fig. 22. Chain of tetranulear $[Au_2M_2]$ (M = Ag, Cu) units

and pyridine arene ligands and to packing effects. Moreover, theoretical calculations based on approximate distances and angles have been carried out, revealing the presence of both metallophilic $Au^I\cdots Ag^I$ and aromatic C_6F_5–py interactions [167].

The rest of Au/Ag materials present a general formula $[Au_2Ag_2(C_6F_5)_4L_2]_n$ (L = 1,10-phen, 2,2′-bipy, tht, O=CMe₂, N≡CMe) and they all seem to be one-dimensional polymers, in accordance with the structures of the acetone [166] and acetonitrile [169] derivatives, recently determined, and to those previously described for other complexes of the same stoichiometry [164,165]. The same stoichiometry and structure is shown in the copper complex $[Au_2Cu_2(C_6F_5)_4(N{\equiv}CMe)_2]_n$, readily synthesized in acetonitrile by reaction of equimolecular amounts of the silver derivative and CuCl in a transmetallation reaction [169] (Eq. (26)).

These three complexes are brightly luminescent in the solid state at room temperature and at 77 K with lifetimes in the nanosecond range. They undergo olygomerization in solution *via* Au···Au interactions as observed through UV–vis and excitation spectra in acetone or acetonitrile solutions at high concentrations. Thus, a correlation between the excitation spectra in solution at different concentrations and the absorption spectra in solid-state can be established. Time-dependent DFT calculations carried out based on models of these systems support the idea that the origin of the luminescence of these complexes stems from orbitals located in the tetranuclear Au_2M_2 units.

If the reaction shown in Eq. (26) is carried out with two equivalents of copper chloride in the presence of one equivalent of pyrimidine, a different type of Au^I/Cu^I organometallic polymer, $[AuCu(C_6F_5)_2(N{\equiv}CMe)(N_2C_4H_4)]_n$, is obtained [170].

$$[Au_2Ag_2(C_6F_5)_4(N{\equiv}CMe)_2]_n \xrightarrow[N\equiv CMe]{CuCl} [Au_2Cu_2(C_6F_5)_4(N{\equiv}CMe)_2]_n \tag{26}$$

Their crystal structures show polymeric chains by repetition of $[Au_2M_2(C_6F_5)_4L_2]$ units through Au···Au contacts ranging form 2.8807(4) to 3.1674(11) Å, and M···M interactions of 3.1810(13) and 3.1084(10) Å are present within the tetranuclear core in the silver derivatives, which are absent in the copper one (Cu–Cu separation 3.0197(11) Å) (see Fig. 22). Each silver or copper atom is bonded to two gold centers with Au–M distances in the range 2.7267(5)–2.7903(9) Å (M = Ag) or of 2.5876(5) and 2.5741(6) Å (M = Cu), which implies a stronger bonding interaction in the silver derivative than in the copper one taking into account the van der Waals radii for the three metals (Cu: 1.40, Ag: 1.72, Au: 1.66 Å) [171]. Although the three structures are very similar, there are some differences in their bonding structure. First, while in the silver complexes all the pentafluorophenyl groups bridge the gold and silver atoms asymmetrically (see Fig. 2a) with Au–C and Ag–C distances in the range 2.055(6)–2.092(7) Å and 2.440(8)–2.687(6) Å, respectively, in the copper species half of the C_6F_5 groups also act as an asymmetric bridge between gold and copper (Au–C and Cu–C distances of 2.043(5) and 2.8642(38) Å, respectively), and the other half bind Au and Cu more symmetrically (see Fig. 22b) with Au–C and Cu–C bond distances of 2.090(4) and 2.141 Å, respectively.

Its crystal structure consists of a polymeric chain formed by the repetition of $[Cu(N_2C_4H_4)]$ units joint together through the bridging pyrimidine ligands, and with the additional coordination of each Cu(I) center to a molecule of acetonitrile and to the gold atom of a linear $[Au(C_6F_5)_2]^-$ unit *via* an unsupported Au···Cu bonding interaction of 2.8216(6) Å (Fig. 23). It is worth noting that this is the first unsupported Au···Cu contact reported,

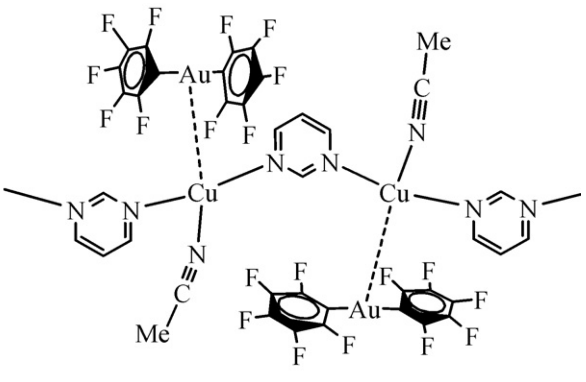
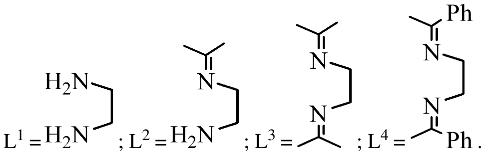


Fig. 23. Chain of $[AuCu(C_6F_5)_2(NCMe)(N_2C_4H_4)]$

Table 4
Gold/thallium complexes

Complex	Au–C (Å)	C–Au–C (°)	Tl–Au–Tl (°)	Au–Tl–Au (°)	M···M (Å)	Au···Tl (Å)	Reference
$[AuTl(C_6F_5)_2]_n$							[172]
$[AuTl(C_6F_5)_2(py_2)]_n$							[175]
$[AuTl(C_6F_5)_2(2,2'\text{-bipy})]_n$	2.064(3)	171.86(14)	140.52(1)	176.08(1)		3.0825(4) 3.1397(4)	[175]
$[AuTl(C_6F_5)_2(1,10\text{-phen})]_n$	2.069(8)	173.2(4)	120.19(2)	120.19(2)		3.0120(6) 3.4899(6)	[175]
$[AuTl(C_6F_5)_2(4,4'\text{-bipy})(THF)]_n$	2.040(6)	177.2(2)	163.24(1)	163.24(1)		3.2155(3) 3.4800(3)	[175]
$[AuTl(C_6F_5)_2(4,4'\text{-bipy})]_n$	2.048(3) 2.049(3)	177.6(1)	$164.92(1)_{[Tl–Au–Au]}$		$3.4092(3)_{Au}$	3.0161(2)	[173]
$[AuTl(C_6F_5)_2(OPPh_3)_2]_n$	2.058(5) 2.053(6)	180.0	180.0	163.1(8)		3.0358(8) 3.0862(8)	[174]
$[AuTl(C_6F_5)_2(L^1)]$							[177]
$[AuTl(C_6F_5)_2(L^2)]_n$							[177]
$[AuTl(C_6F_5)_2(L^3)]_n$	2.045(6) 2.047(6)	180.0	180.0	139.20(1)		3.0479(2) 3.1427(2)	[177]
$[AuTl(C_6F_5)_2(L^4)]_n$							[177]
$[Au_2Tl_2(C_6F_5)_4(\mu\text{-DMSO})_3]_n$	2.057(8) 2.060(8)	179.1(4) 179.9(4)	178.82(2)	67.09(2)	$[4.100]_{Tl}$	3.2225(6) 3.2465(6) 3.5182(8)	[176]
$[AuTl_3(C_6F_5)_2(acac)_2]_n$	2.047(5)	177.3(3)	$165.07(1)_{[Tl–Tl–Tl]}$ $97.91(1)_{[Tl–Tl–Tl]}$ $97.02(1)_{[Tl–Tl–Tl]}$ $82.87(1)_{[Tl–Tl–Tl]}$ $82.19(1)_{[Tl–Tl–Tl]}$		$3.6688(4)_{Tl}$ $3.7200(4)_{Tl}$ $3.7607(4)_{Tl}$	3.0653(4)	[172]



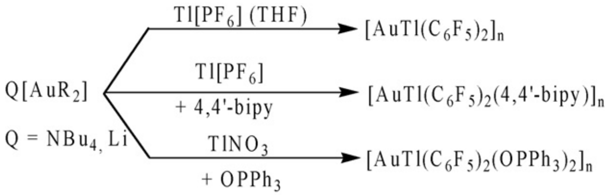
since the intramolecular Au···Au separation is longer than 6 Å and no additional secondary interactions were detected.

The strong luminescence observed in the pyrimidine derivative, which has a rich photophysics in solution and in the solid state, is tentatively assigned to a LMCT phosphorescent process. This result is interpreted in terms of the Lewis basic character of the gold center interacting with the Cu(I) Lewis acid, which favors the copper to pyrimidine charge transfer transition [170].

6.2.2. *Au/Tl complexes*

The acid–base synthetic strategy has also been used to isolate heterometallic Au^I/Tl^I polymeric systems, and thus by reacting equimolecular amounts of bis(pentahalophenyl)aurate(I) and thallium(I) hexafluorophosphate in tetrahydrofuran high yields of the complex $[AuTl(C_6F_5)_2]_n$ are obtained [172]. If this reaction is carried out in the presence of N- or O-donor ligands, such as 4,4′-bipy [173] or $OPPh_3$ [174], the neutral ligand is incorporated in the coordination sphere of the thallium atoms, affording $[AuTl(C_6F_5)_2(4,4'\text{-bipy})]_n$ or $[AuTl(C_6F_5)_2(OPPh_3)_2]_n$, respectively, as shown in Scheme 32.

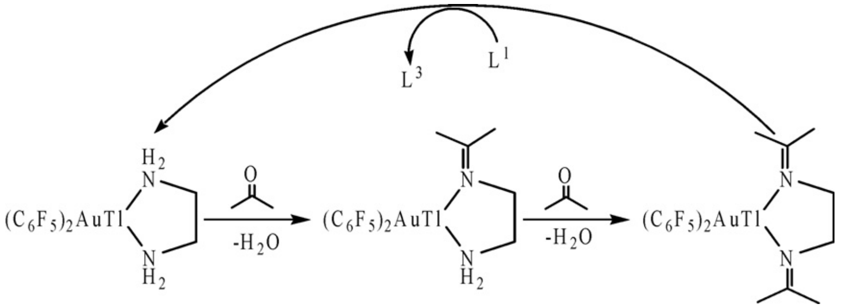
The heteropolynuclear complex $[AuTl(C_6F_5)_2]_n$ also reacts with organic molecules such as pyridine, bipyridine, phenanthroline, dimethysulfoxide or ethylenediamine in the adequate proportions to give materials of the type $[AuTl(C_6F_5)_2L_2]_n$, $[AuTl(C_6F_5)_2(L–L)]_n$ or $[Au_2Tl_2(C_6F_5)_4(\mu\text{-DMSO})_3]_n$ [175–177] or with metal compounds, such as thallium acetylacetonate (1:1) to afford $[AuTl_3(C_6F_5)_2(acac)_2]_n$ [172] (see Table 4).



Scheme 32.

Treatment of the ethylenediamine derivative $[AuTl(C_6F_5)_2(L^1)]$ with ketones at room temperature yields stable amine–imine or diimine complexes (see Scheme 33); these reactions occur in a few seconds even when the solid-state precursor is exposed to ketone vapors [177]. This reactivity contrasts with the classical synthesis of imines, which requires high temperatures, prolonged reaction periods and the presence of dehydrating agents [178–181], and opens the door for the study of new potential applications of heterometallic systems and their use as reagents in organic synthesis.

The crystal structures of most of these species have been determined and their polymeric nature has been confirmed thanks to the presence of unsupported interactions between the closed-shell metal ions (Au^I and Tl^I) with Au–Tl distances in the range 3.0120(6)–3.5182(8) Å. The crystal structures of the



Scheme 33.

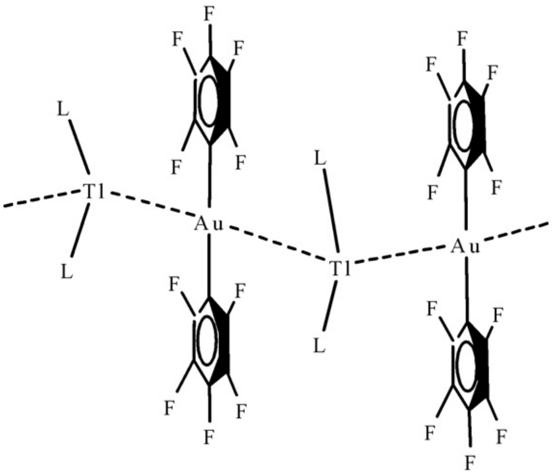


Fig. 24. Chain of $[AuTl(C_6F_5)_2L_2]$

diimine ligand L^3, 2,2′-bipyridine, 1,10-phenantroline or $OPPh_3$ show one-dimensional chains with alternating square-planar Au^I and distorted trigonal bipyramidal Tl^I centers (considering the intermetallic contacts) with a vacant equatorial coordination site apparently associated with the stereochemically active lone pair and the gold centers occupying the apical positions (Fig. 24).

In the case of $[AuTl(C_6F_5)_2(4,4'\text{-bipy})(THF)]_n$, the bidentate ligands act as bridges between Tl^I centers of adjacent chains, resulting in a 2D-network represented in Fig. 25. Interestingly, this structure displays an unusual distorted octahedral environment for the thallium atoms, which, besides the Au···Tl contacts, bind two nitrogen atoms, the oxygen of a THF molecule and interact with a fluorine atom of an adjacent layer. Considering this Tl···F contacts the structure can be described as a three-dimensional polymer [175].

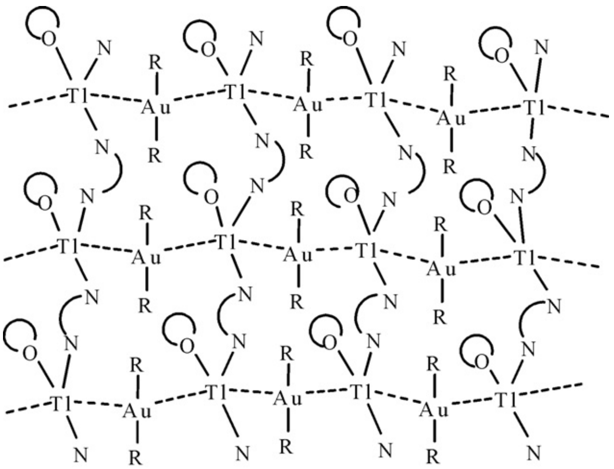


Fig. 25. 2D structure of $[AuTl(C_6F_5)_2(4,4\text{-bipy})(THF)]$

The 4,4′-bipyridine derivative is formed by tetranuclear units with an unusual sequence Tl–Au–Au–Tl, where repulsive instead of attractive forces could be expected, linked through bridging bipyridine ligands forming planar polymers (see Fig. 26). If additional Tl···F contacts that connect adjacent planes are taken into account, the structure of this complex can be seen as an infinite 3D polymer [173].

The solid-state structure of the product with DMSO (DMSO = dimethylsulfoxide) as ligand, which exhibits a different stoichiometry, can be viewed as an extended linear chain built by the repetition of $[\cdots(C_6F_5)_2Au\cdots Tl\text{–}(\mu\text{-DMSO})_3\text{–}Tl\cdots]$ units linked *via* both unsupported Au···Tl interactions and bridging DMSO molecules bonded to thallium, and with an additional terminal $[Au(C_6F_5)_2]^-$ fragment interacting with one of the thallium centers (Fig. 27) [176].

Finally, the crystal structure of the acetylacetonate derivative $[AuTl_3(C_6F_5)_2(acac)_2]_n$, which presents a different Au/Tl ratio than the other complexes, contains $Tl_2(acac)_2$ and $[AuTl(C_6F_5)_2]$ units linked *via* two Tl–O bonds [172]. Polymerization occurs as a consequence of the presence of unsupported Tl···Tl contacts of 3.7200(4) and 3.7607(4) Å, and each $Tl_2(acac)_2$ unit links one $[AuTl(C_6F_5)_2]$ unit forming a double-chain one-dimensional polymer (Fig. 28), while in the related pentachlorophenyl complex $[AuTl_2(C_6Cl_5)_2(acac)]_n$ each $Tl_2(acac)_2$ unit links two $[AuTl(C_6F_5)_2]$ units and forms a two-dimensional network [172]. The thallium atoms in the $Tl_2(acac)_2$ units display a Tl···Tl contact of 3.6688(4) Å.

All these Au/Tl complexes are strongly luminescent in the solid state both at room temperature and at 77 K, showing a temperature-dependence that is assumed to be a result of the thermal contraction that occurs when temperature is lowered, generally losing this characteristic in solution. This luminescence, which is also affected by the structural arrangements, can therefore be attributed to intermetallic interactions, which is also suggested by the DFT calculations that reveal the metallic nature of the orbitals involved in each transition [173].

When Tl···Tl contacts are present in addition to the Au···Tl ones, the luminescence remains in solution. The comparison

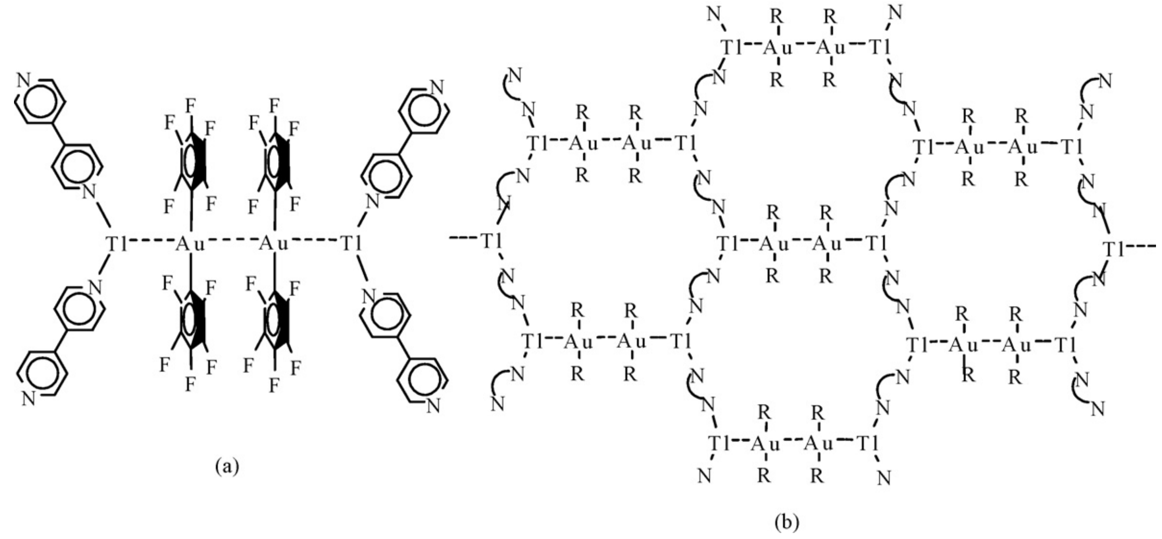


Fig. 26. 2D structure of [AuTl$(C_6F_5)_2$(4,4-bipy)]

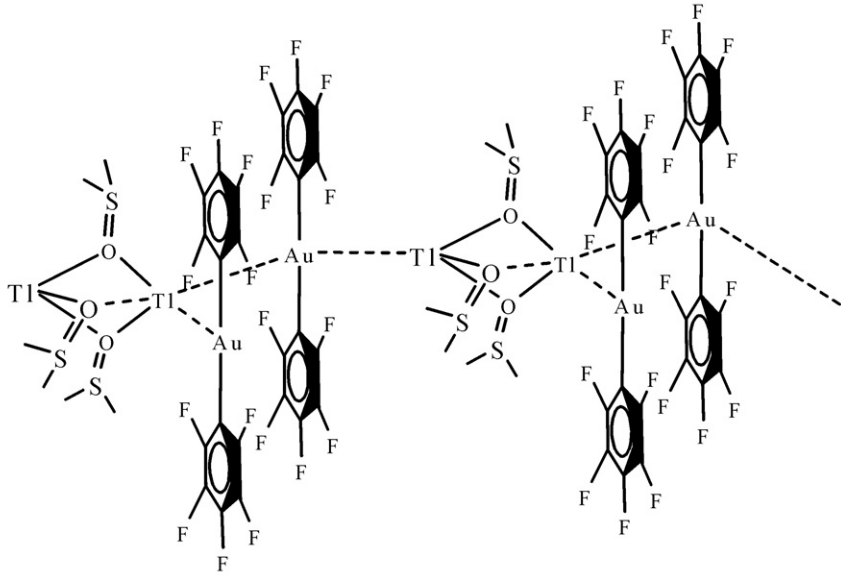


Fig. 27. Chain of $[Au_2Tl_2(C_6F_5)_4(DMSO)_3]$

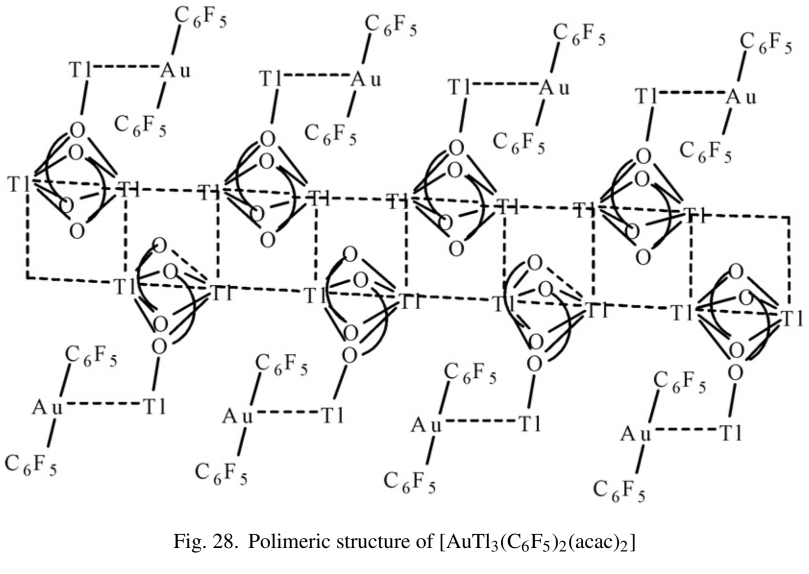


Fig. 28. Polimeric structure of $[AuTl_3(C_6F_5)_2(acac)_2]$

of these properties in solution with that of Tl(acac) seems to indicate that the Tl···Tl interactions are not broken when the products are dissolved. Thus, both the Au···Tl and Tl···Tl interactions are considered to be responsible for luminescence in solid state, while experimental observations and TD-DFT calculations show that the $Tl_2(acac)_2$ unit would be responsible for the luminescent behavior in solution [172].

7. Summary

As a conclusion, pentafluorophenyl groups confer a great stability on metal complexes and make then much more stable than their corresponding phenyl derivatives. This has allowed the synthesis and isolation of a high number of compounds, mainly gold(I) and gold(III) derivatives, which include homo and heterometal species and that can also contain neutral or anionic ligands with a great variety of donor atoms, including some ferrocene derivatives as non-classical ligands. The stability of the anion bis(perfluorophenyl)aurate(I) is so high that it can even be used as a metalloligand in acid–base reactions against Lewis acids, such as silver(I), copper(I) or thallium(I) salts, which lead to supramolecular arrays with potential applications and in which metal–metal interactions are frequent, and are often the responsible for their interesting photophysical properties.

References

[1] W.P. Pope, C.S. Gibson, J. Chem. Soc. (1907) 2061.
[2] W.P. Pope, C.S. Gibson, Proc. Chem. Soc. 23 (1908) 245.
[3] B. Armer, H. Schmidbaur, Angew. Chem. Int. Ed. Engl. 9 (1970) 101.
[4] H. Schmidbaur, Angew. Chem. Int. Ed. Engl. 15 (1976) 728.
[5] R. Usón, A. Laguna, J. Vicente, Synth. React. Inorg. Metal -Org. Chem. 7 (1977) 463.
[6] H. Schmidbaur, Gmelin Handbuch der Anorganischen Chemie. Organogold Compounds, Springer Verlag, Berlin, 1980.
[7] G.K. Anderson, Adv. Organometall. Chem. 20 (1982) 39.
[8] R.V. Parish, Gold Bull. 30 (1997) 3;
R.V. Parish, Gold Bull. 30 (1997) 55;
R.V. Parish, Gold Bull. 31 (1998) 14.
[9] H. Schmidbaur, A. Grohmann, M.E. Olmos, Gold: progress in chemistry, biochemistry and technology, in: Organogold Chemistry, J. Wiley & Sons, Chichester, 1999.
[10] H. Schmidbaur, A. Grohmann, M.E. Olmos, A. Schier, The Chemistry of Organic Derivatives of Gold and Silver. Synthesis and Uses of Organogold Compounds, J. Wiley & Sons, Chichester, 1999.
[11] R. Usón, A. Laguna, Coord. Chem. Rev. 70 (1986) 1.
[12] R. Usón, Pure Appl. Chem. 58 (1986) 647.
[13] R. Usón, J. Organometall. Chem. 372 (1989) 171.
[14] A. Laguna, M.C. Gimeno, Trends Organometall. Chem. 1 (1994) 231.
[15] E.J. Fernández, A. Laguna, M.E. Olmos, Adv. Organometall. Chem. 52 (2005) 77.
[16] J. Vicente, M.T. Chicote, P. González-Herrero, K. Grünwald, P.G. Jones, Organometallics 16 (1997) 3381.
[17] O. Schuster, H. Schmidbaur, Z. Naturfosch. 61b (2006) 961.
[18] R. Usón, A. Laguna, Organometall. Synth. 3 (1989) 342.
[19] P.G. Jones, M.D. Villacampa, Z. Krist.: New Cryst. Struct. 212 (1997) 121.
[20] D.A. Briggs, R.G. Raptis, J.P. Fackler Jr., Acta Crystallogr. C44 (1988) 1313.
[21] R. Usón, A. Laguna, M. Laguna, E.J. Fernández, M.D. Villacampa, P.G. Jones, G.M. Sheldrick, J. Chem. Soc., Dalton Trans. (1983) 1679.
[22] M. Bardají, A. Laguna, M.D. Villacampa, Acta Crystallogr. C56 (2000) e487.
[23] E. Cerrada, M. Laguna, J. Bartolomé, J. Campo, V. Orera, P.G. Jones, Synth. Metals 92 (1998) 245.
[24] U. Koelle, A. Laguna, Inorg. Chim. Acta 290 (1999) 44.
[25] R. Casado, M. Contel, M. Laguna, P. Romero, S. Sanz, J. Am. Chem. Soc. 125 (2003) 11925.
[26] A. Adé, E. Cerrada, M. Contel, M. Laguna, P. Merino, T. Tejero, J. Organometall. Chem. 689 (2004) 1788.
[27] P.G. Jones, G.M. Sheldrick, E. Hädicke, Acta Crystallogr. B36 (1980) 2777.
[28] H. Schmidbaur, A. Kolb, E. Zeller, A. Schier, H. Beruda, Z. Anorg. Allg. Chem. 619 (1993) 1575.
[29] K. Angermaier, H. Schmidbaur, Chem. Ber. 127 (1994) 2387.
[30] P.G. Jones, C. Lensch, G.M. Sheldrick, Z. Naturforsch. 37B (1982) 141.
[31] P. Pyykkö, K. Angermaier, B. Assmann, H. Schmidbaur, J. Chem. Soc., Chem. Commun. (1995) 1889.
[32] F. Canales, S. Canales, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, Organometallics 17 (1998) 1617.
[33] F. Canales, M.C. Gimeno, A. Laguna, P.G. Jones, J. Am. Chem. Soc. 118 (1996) 4839.
[34] F. Canales, M.C. Gimeno, A. Laguna, P.G. Jones, Organometallics 15 (1996) 3412.
[35] M.J. Calhorda, F. Canales, M.C. Gimeno, J. Jiménez, P.G. Jones, A. Laguna, L.F. Veiros, Organometallics 16 (1997) 3837.
[36] S. Canales, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, F. Mendizabal, Organometallics 20 (2001) 4812.
[37] F. Canales, M.C. Gimeno, P.G. Jones, A. Laguna, Angew. Chem. Int. Ed. Engl. 33 (1994) 769.
[38] F. Canales, M.C. Gimeno, A. Laguna, M.D. Villacampa, Inorg. Chim. Acta 244 (1996) 95.
[39] P.G. Jones, C. Lensch, G.M. Sheldrick, Z. Naturforsch. 37B (1982) 944.
[40] S. Canales, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, F. Mendizabal, Organometallics 19 (2000) 4985.
[41] P.G. Jones, C. Thöne, Z. Naturforsch. 46B (1990) 50.
[42] See for example:
W.E. Smith, J. Reglinski, Perpesct. Bioinorg. Chem. 1 (1991) 183.
[43] O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, M.D. Villacampa, J. Chem. Soc., Dalton Trans. (1997) 2963.
[44] M. Bardají, M.J. Calhorda, P.J. Costa, P.G. Jones, A. Laguna, M.R. Pérez, M.D. Villacampa, Inorg. Chem. 45 (2006) 1059.
[45] O. Crespo, F. Canales, M.C. Gimeno, P.G. Jones, A. Laguna, Organometallics 18 (1999) 3142.
[46] S. Canales, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, Inorg. Chem. 43 (2004) 7234.
[47] E. Cerrada, P.G. Jones, A. Laguna, M. Laguna, Inorg. Chem. 35 (1996) 2995.
[48] O. Crespo, M.C. Gimeno, P.G. Jones, B. Ahrens, A. Laguna, Inorg. Chem. 36 (1997) 495.
[49] O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, J. Organometall. Chem. 547 (1997) 89.
[50] E. Cerrada, E.J. Fernández, M.C. Gimeno, A. Laguna, M. Laguna, R. Terroba, M.D. Villacampa, J. Organometall. Chem. 492 (1995) 105.
[51] R. Terroba, E.J. Fernández, M.B. Hursthouse, M. Laguna, Polyhedron 17 (1998) 2433.
[52] E. Cerrada, E.J. Fernández, P.G. Jones, A. Laguna, M. Laguna, R. Terroba, Organometallics 14 (1995) 5537.
[53] P.G. Jones, E.Z. Bembenek, Z. Kristallogr. 209 (1994) 690.
[54] R. Usón, A. Laguna, J. Vicente, J. García, P.G. Jones, G.M. Sheldrick, J. Chem. Soc., Dalton Trans. (1981) 655.
[55] R. Usón, A. Laguna, M. Laguna, M.L. Castilla, P.G. Jones, K. Meyer-Bäse, J. Chem. Soc. 336 (1987) 453.
[56] A. Laguna, M. Laguna, J. Jimenez, F.J. Lahoz, E. Olmos, J. Organometall. Chem. 435 (1992) 235.
[57] J.H. Noordik, P.T. Beurskens, J. Cryst. Mol. Cryst. 1 (1971) 339.
[58] M. Nakamoto, H. Koijman, M. Paul, W. Hiller, H. Schmidbaur, Z. Anorg. Allg. Chem. 619 (1993) 1341.
[59] M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, R. Terroba, Inorg. Chem. 33 (1994) 3932.

[60] G. Bandoli, D.A. Clemente, G. Marangoni, L. Cattalini, J. Chem. Soc., Dalton Trans. (1973) 886.
[61] J. Stein, J.P. Fackler Jr., C. Paparizos, H.W. Chen, J. Am. Chem. Soc. 103 (1981) 2192.
[62] U. Grässle, J. Strähle, Z. Anorg. Allg. Chem. 531 (1985) 26.
[63] D. Coucouvanis, Prog. Inorg. Chem. 11 (1970) 233.
[64] G.D. Thorn, R.A. Ludwig, The Dithiocarbamates and Related Compounds, Elsevier, Amsterdam, 1962.
[65] J.J. Criado, J.A. López-Arias, B. Macías, L.R. Fernández-Lago, J.M. Salas, Inorg. Chim. Acta 193 (1992) 229, and references therein.
[66] E.J. Fernández, J.M. López de Luzuriaga, M. Monge, E. Olmos, A. Laguna, M.D. Villacampa, P.G. Jones, J. Clust. Sci. 11 (2000) 153.
[67] M. Bardají, A. Laguna, P.G. Jones, A.K. Fischer, Inorg. Chem. 39 (2000) 3560.
[68] M. Bardají, A. Blasco, J. Jiménez, P.G. Jones, A. Laguna, M. Laguna, F. Merchán, Inorg. Chim. Acta 223 (1994) 55.
[69] M. Bardají, A. Laguna, M. Laguna, F. Merchán, Inorg. Chim. Acta 215 (1994) 215.
[70] M.C. Gimeno, E. Jambrina, A. Laguna, M. Laguna, H.H. Murray, R. Terroba, Inorg. Chim. Acta 249 (1996) 69.
[71] S. Cronje, H.G. Raubenheimer, H.S.C. Spies, C. Esterhuysen, H. Schmidbaur, A. Schier, G.J. Kruger, Dalton Trans. (2003) 2859.
[72] T. Mathieson, A. Schier, H. Schmidbaur, J. Chem. Soc., Dalton Trans. (2001) 1196.
[73] R. Usón, A. Laguna, J. Vicente, J. Chem. Soc., Chem. Commun. (1976) 353.
[74] R. Usón, A. Laguna, M. Laguna, Inorg. Synth. 26 (1989) 87.
[75] J. Coetzee, W.F. Gabrielli, K. Coetzee, O. Schuster, S.D. Nogai, S. Cronje, H.G. Raubenheimer, Angew. Chem. Int. Ed. 46 (2007) 2497.
[76] R. Usón, A. Laguna, M. Laguna, M.L. Castilla, P.G. Jones, C. Fittschen, J. Chem. Soc., Dalton Trans. (1987) 3017.
[77] F. Mohr, E. Cerrada, M. Laguna, Organometallics 25 (2006) 644.
[78] S.A. Yurin, D.A. Lemenovskii, K.I. Grandgerb, I.G. Ll'ina, L.G. Kuz'mina, Russ. Chem. Bull. Int. Ed. 52 (2003) 2752.
[79] V.W.W. Yam, S.W.K. Choi, K.K. Cheung, Chem. Commun. (1996) 1173.
[80] V.W.W. Yam, C.K. Li, C.L. Chan, K.K. Cheung, Inorg. Chem. 40 (2001) 7054.
[81] S. Canales, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, Z. Naturforsch. 62B (2007) 407.
[82] P.A. Bella, O. Crespo, E.J. Fernández, A.K. Fischer, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, J. Chem. Soc., Dalton Trans. (1999) 4009.
[83] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, E. Olmos, J. Chem. Soc., Dalton Trans. (1997) 3515.
[84] S. Canales, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, A. Silvestru, C. Silvestru, Inorg. Chim. Acta 347 (2003) 16.
[85] B. Alvarez, E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, Polyhedron 17 (1998) 2029.
[86] H. Schmidbaur, R. Herr, G. Müller, J. Riede, Organometallics 4 (1985) 1208.
[87] R. Usón, A. Laguna, M. Laguna, I. Lázaro, P.G. Jones, Organometallics 6 (1987) 2326.
[88] A. Codina, E.J. Fernández, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, M.E. Olmos, J. Pérez, M.A. Rodríguez, J. Am. Chem. Soc. 124 (2002) 6781.
[89] P.G. Jones, B. Ahrens, Z. Naturfosch. 53b (1998) 653.
[90] S. Bordoni, L. Busetto, M.C. Cassani, V.G. Albano, P. Sabatino, Inorg. Chim. Acta 222 (1994) 267.
[91] M. Bardají, A. Laguna, M.R. Pérez, P.G. Jones, Organometallics 21 (2002) 1877.
[92] J.J. Guy, P.G. Jones, M.J. Mays, G.M. Sheldrick, J. Chem. Soc., Chem. Commun. (1977) 8.
[93] M. Albrecht, K. Hübler, W. Kaim, Z. Naturfosch. 54b (1999) 1606.
[94] M. Desmet, H.G. Raubenheimer, G.J. Kruger, Organometallics 17 (1997) 3324.
[95] K. Nomiya, R. Noguchi, K. Ohsawa, K. Tsuda, M. Oda, J. Inorg. Biochem. 78 (2000) 363.
[96] P. Byabartta, Transit. Metal Chem. 32 (2007) 314.
[97] M.C. Blanco, E.J. Fernández, J.M. López-de-Luzuriaga, M.E. Olmos, O. Crespo, M.C. Gimeno, A. Laguna, P.G. Jones, Chem. Eur. J. 6 (2000) 4116.
[98] M.C. Blanco, E.J. Fernández, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, M.E. Olmos, Angew. Chem. Int. Ed. Engl. 37 (1998) 3042.
[99] M.C. Blanco, E.J. Fernández, M.E. Olmos, J. Pérez, O. Crespo, A. Laguna, P.G. Jones, Organometallics 23 (2004) 4373.
[100] M.C. Blanco, E.J. Fernández, M.E. Olmos, J. Pérez, A. Laguna, Chem. Eur. J. 12 (2006) 3379.
[101] M.C. Blanco, E.J. Fernández, A.K. Fischer, P.G. Jones, A. Laguna, M.E. Olmos, M.D. Villacampa, Inorg. Chem. Commun. 3 (2000) 163.
[102] A. Bayler, A. Schier, G.A. Bowmaker, H. Schmidbaur, J. Am. Chem. Soc. 118 (1996) 7006.
[103] M.C. Blanco, E.J. Fernández, M.E. Olmos, O. Crespo, A. Laguna, P.G. Jones, Organometallics 21 (2002) 2426.
[104] M. Bardají, P.G. Jones, A. Laguna, J. Chem. Soc., Dalton Trans. (2002) 3624.
[105] O. Crespo, E.J. Fernández, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, M.E. Olmos, J. Pérez, J. Chem. Soc., Dalton Trans. (2003) 1076.
[106] E.J. Fernández, J.M. López-de-Luzuriaga, M. Monge, M.A. Rodríguez, O. Crespo, M.C. Gimeno, A. Laguna, P.G. Jones, Chem. Eur. J. 6 (2000) 636.
[107] C. Hollatz, A. Schier, H. Schmidbaur, Z. Naturfosch. 54b (1999) 30.
[108] P.G. Jones, R. Terroba, E. Fernández, M. Laguna, Acta Crystallogr. E58 (2002) m90.
[109] E.J. Fernández, M. Gil, M.E. Olmos, O. Crespo, A. Laguna, P.G. Jones, Inorg. Chem. 40 (2001) 3018.
[110] M. Bardají, P.G. Jones, A. Laguna, Organometallics 20 (2001) 3906.
[111] P.G. Jones, E.J. Fernández, J.M. López-de-Luzuriaga, A. Laguna, Acta Crystallogr. E62 (2006) m1997.
[112] M. Bardají, P.G. Jones, A. Laguna, M.D. Villacampa, N. Villaverde, J. Chem. Soc., Dalton Trans. (2003) 4529.
[113] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, E. Olmos, Chem. Ber. 130 (1997) 1513.
[114] M. Bardají, M.T. de la Cruz, P.G. Jones, A. Laguna, J. Martínez, M.D. Villacampa, Inorg. Chim. Acta 358 (2005) 1365.
[115] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, E. Olmos, Organometallics 16 (1997) 1130.
[116] M.A. Bennett, D.C.R. Hockless, A.D. Rae, L.L. Welling, A.C. Willis, Organometallics 20 (2001) 79.
[117] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, J.M. López-de-Luzuriaga, Organometallics 14 (1995) 2918.
[118] M. Bardají, A. Laguna, J. Vicente, P.G. Jones, Inorg. Chem. 40 (2001) 2675.
[119] M. Bardají, A. Laguna, V.M. Orera, M.D. Villacampa, Inorg. Chem. 37 (1998) 5125.
[120] E.J. Fernández, M.C. Gimeno, A. Laguna, M. Laguna, J.M. López-de-Luzuriaga, E. Olmos, J. Organometall. Chem. 514 (1996) 169.
[121] E.J. Fernández, M.C. Gimeno, P.G. Jones, B. Ahrens, A. Laguna, M. Laguna, J.M. López-de-Luzuriaga, J. Chem. Soc., Dalton Trans. (1994) 3487.
[122] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, E. Olmos, J. Chem. Soc., Dalton Trans. (1996) 3603.
[123] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, E. Olmos, J. Chem. Soc., Dalton Trans. (1994) 2891.
[124] A. Laguna, M. Laguna, J. Organometall. Chem. 394 (1990) 743, and references therein.
[125] H. Schmidbaur, A. Stützer, E. Herdtweck, Chem. Ber. 124 (1991) 1095.
[126] E.J. Fernández, M.C. Gimeno, A. Laguna, J.M. López-de-Luzuriaga, E. Olmos, Polyhedron 17 (1998) 3919.
[127] M.C. Gimeno, J. Jiménez, P.G. Jones, A. Laguna, M. Laguna, Organometallics 13 (1994) 2508.
[128] M.A. Bennett, S.K. Bhargava, F. Mohr, L.L. Welling, A.C. Willis, Aust. J. Chem. 55 (2002) 267.
[129] B. Alvarez, E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, J.M. López-de-Luzuriaga, J. Organometall. Chem. 525 (1996) 109.

[130] E.J. Fernández, J.M. López-de-Luzuriaga, M. Monge, M.A. Rodríguez, O. Crespo, M.C. Gimeno, A. Laguna, P.G. Jones, Inorg. Chem. 37 (1998) 6002.
[131] M. Jansen, Angew. Chem. Int. Ed. Engl. 26 (1987) 1098.
[132] E.J. Fernández, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, M. Montiel, M.E. Olmos, M. Rodríguez-Castillo, Dalton Trans. (2006) 3672.
[133] E.J. Fernández, M.B. Hursthouse, M. Laguna, R. Terroba, J. Organometall. Chem. 574 (1999) 207.
[134] X. Hong, K.K. Cheung, C.X. Guo, C.-M. Che, J. Chem. Soc., Dalton Trans. (1994) 1867.
[135] P.G. Jones, C. Thöne, Acta Crystallogr. C 48 (1992) 1312.
[136] H.G. Raubenheimer, F. Scott, G.J. Kruger, J.G. Toerien, R. Otte, W. van Zyl, I. Taljaard, P. Olivier, L. Lindford, J. Chem. Soc., Dalton Trans. (1994) 2091.
[137] H.G. Raubenheimer, M. Desmet, G.J. Kruger, J. Chem. Soc., Dalton Trans. (1995) 2067.
[138] V.G. Albano, L. Busetto, M.C. Cassani, P. Sabatino, A. Schmitz, V. Zanotti, J. Chem. Soc., Dalton Trans. (1995) 2087.
[139] A. Olin, Acta Chem. Scand. Ser. A 14 (1960) 126.
[140] H. Lang, K. Köhler, L. Zsolnai, Chem. Commun. (1996) 2043.
[141] K. Köhler, S.J. Silverio, I. Hyla-Kryspin, R. Gleiter, L. Zsolnai, A. Driess, G. Huttner, H. Lang, Organometallics 16 (1997) 4970.
[142] J. Vicente, M.T. Chicote, M.D. Abrisqueta, P.G. Jones, Organometallics 19 (2000) 2629.
[143] I. Romeo, M. Bardají, M.C. Gimeno, M. Laguna, Polyhedron 19 (2000) 1837.
[144] R. Usón, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones, G.M. Sheldrick, J. Chem. Soc., Dalton Trans. (1984) 839.
[145] R. Usón, A. Laguna, M. Laguna, M.C. Gimeno, P.G. Jones, C. Fittschen, G.M. Sheldrick, J. Chem. Soc., Chem. Commun. (1986) 509.
[146] R. Usón, A. Laguna, M. Laguna, I. Lázaro, A. Morata, P.G. Jones, G.M. Sheldrick, J. Chem. Soc., Dalton Trans. (1986) 669.
[147] A. Laguna, M. Laguna, J. Jiménez, F.J. Lahoz, E. Olmos, Organometallics 13 (1994) 253.
[148] A. Togni, T. Hayashi (Eds.), Ferrocenes, Homogeneous Catalysis, Organic Synthesis and Material Science, VCH, Weinheim, 1995.
[149] A. Togni, R.L. Halterman (Eds.), Metallocenes, VCH, Weinheim, 1998.
[150] N.J. Long, Metallocenes, Blackwell, Oxford, 1998.
[151] E.M. Barranco, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, M.D. Villacampa, J. Organometall. Chem. 592 (1999) 258.
[152] E.M. Barranco, M.C. Gimeno, A. Laguna, M.D. Villacampa, Inorg. Chim. Acta 358 (2005) 4177.
[153] E.M. Barranco, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, Eur. J. Inorg. Chem. (2004) 4820.
[154] E.M. Barranco, O. Crespo, M.C. Gimeno, A. Laguna, P.G. Jones, B. Ahrens, Inorg. Chem. 39 (2000) 680.
[155] J.E. Aguado, S. Canales, M.C. Gimeno, P.G. Jones, A. Laguna, M.D. Villacampa, Dalton Trans. (2005) 3005.
[156] E.M. Barranco, M.C. Gimeno, A. Laguna, Inorg. Chim. Acta 291 (1999) 60.
[157] M.C. Gimeno, P.G. Jones, A. Laguna, C. Sarroca, J. Organometall. Chem. 579 (1999) 206.
[158] M. Viotte, B. Gautheron, M.M. Kubicki, Y. Mugnier, R.V. Parish, Inorg. Chem. 34 (1995) 3465.
[159] E.M. Barranco, O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, C. Sarroca, J. Chem. Soc., Dalton Trans. (2001) 2523.
[160] M.C. Gimeno, P.G. Jones, A. Laguna, C. Sarroca, J. Organometall. Chem. 596 (2000) 10.
[161] J.E. Aguado, M.J. Calhorda, M.C. Gimeno, A. Laguna, Chem. Commun. (2005) 3355.
[162] M.C. Gimeno, P.G. Jones, A. Laguna, C. Sarroca, M.J. Calhorda, L.F. Veiros, Chem. Eur. J. 4 (1998) 2308.
[163] S. Canales, O. Crespo, A. Fortea, M.C. Gimeno, P.G. Jones, A. Laguna, Dalton Trans. (2002) 2255.
[164] R. Usón, A. Laguna, M. Laguna, P.G. Jones, G.M. Sheldrick, J. Chem. Soc., Chem. Commun. (1981) 1097.
[165] R. Usón, A. Laguna, M. Laguna, B.R. Manzano, P.G. Jones, G.M. Sheldrick, J. Chem. Soc., Dalton Trans. (1984) 285.
[166] E.J. Fernández, M.C. Gimeno, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, P. Pyykkö, D. Sundholm, J. Am. Chem. Soc. 122 (2000) 7287.
[167] E.J. Fernández, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, P. Pyykkö, N. Runeberg, Eur. J. Inorg. Chem. (2002) 750.
[168] A. Luquin, C. Bariáin, E. Vergara, E. Cerrada, J. Garrido, I.R. Matias, M. Laguna, Appl. Organometall. Chem. 19 (2005) 1232.
[169] E.J. Fernández, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, M. Montiel, M.E. Olmos, M. Rodríguez-Castillo, Organometallics 25 (2006) 3639.
[170] E.J. Fernández, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, M. Montiel, M.E. Olmos, Inorg. Chem. 44 (2005) 1163.
[171] http://www.webelements.com.
[172] E.J. Fernández, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, M. Montiel, M.E. Olmos, J. Pérez, Organometallics 23 (2004) 774.
[173] E.J. Fernández, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, M.E. Olmos, J. Pérez, Inorg. Chem. 41 (2002) 1056.
[174] O. Crespo, E.J. Fernández, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, A. Mendía, M. Monge, M.E. Olmos, Chem. Commun. (1998) 2233.
[175] E.J. Fernández, P.G. Jones, A. Laguna, J.M. López-de-Luzuriaga, M. Monge, M. Montiel, M.E. Olmos, J. Pérez, Z. Naturforsch. 39b (2004) 1379.
[176] E.J. Fernández, A. Laguna, J.M. López-de-Luzuriaga, M. Montiel, M.E. Olmos, J. Pérez, Inorg. Chim. Acta 358 (2005) 4293.
[177] E.J. Fernández, A. Laguna, J.M. López-de-Luzuriaga, M. Montiel, M.E. Olmos, J. Pérez, Organometallics 25 (2006) 1689.
[178] K. Taguchi, F.H. Westheimer, J. Org. Chem. 36 (1971) 1570.
[179] B.E. Love, J. Ren, J. Org. Chem. 58 (1993) 5556.
[180] G.C. Look, M.M. Murphy, D.A. Campbell, M.A. Gallop, Tetrahedron Lett. 36 (1995) 2937.
[181] R.S. Vaas, J. Duda's, R.S. Varma, Tetrahedron 40 (1999) 4951.