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The 'acac method' for the synthesis of coordination and organometallic compounds: synthesis of gold complexes

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Contents

Abstract

In this review we show the synthetic utility of acetylacetonatogold complexes as reagents for preparing gold(III) complexes with C, N and O donor ligands and gold(I) complexes with

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phosphorus ylide, methanide, methanediide, sulfur ylide, amino, amido, nitrido alkyl, phosphido, thiolato, hydrosulfido, trithiocarbonato, dithiocarbamato, 1,1 dithiolato and alkynyl (including ethynyl) ligands.

Keywords: Gold complexes; Acetylacetonato; Ylide; Thiolato; Hydrosulfido; Trithiocarbonato; Dithiocarbamato; Dithiolato; Alkynyl; Ethynyl

Nomenclature

acac	acetylacetonato
$BiBzImH_2$	2,2′-bibenzimidazole
bipy	2,2′-bipyridine
COD	cycloocta-1,5-diene
Cy	cyclohexyl
dppm	bis(diphenylphosphino)methane
nbd	norborna-2,5-diene
phen	1,10-phenanthroline
ppn	$Ph_3P{=}N{=}PPh_3$
py-2	2-pyridyl
tfb	tetrafluorobenzobarrelene
tht	tetrahydrothiophene
pmp	*para*-methoxyphenyl
To	*para*-Tolyl

1. Introduction

Acetylacetonato (acac) is a classical ligand in coordination chemistry [1,2]. The chemistry of acac complexes has mainly been focused on their reactions with Lewis bases showing the conversion of the chelating *O*,*O*′-acac form into other coordination modes of this ligand [3,4] and on electrophilic substitution reactions giving 3-carbon substituted acac complexes [1].

In this review we report the results we have obtained in the study of the reactivity of acac gold(I) and gold(III) complexes with protic acids. These acid–base reactions have allowed us to prepare many different types of coordination (including organometallic) gold complexes. Previous studies on this subject were limited to reactions of acac complexes with hydrogen halides, alcohols or carboxylic acids [1].

Since 1979, we prepared a family of neutral and cationic heterocyclic gold(III) complexes using an acac complex as a starting material, and showed the versatility

of acac gold complexes for the synthesis of many gold(I) and gold(III) complexes. We find it appropriate to report this synthetic method in this issue of Coordination Chemistry Reviews devoted to the research of Spanish chemists as this approach has mainly been developed by Spanish chemists from the school of Professor Usón in Zaragoza University. We will also refer briefly to the work of these colleagues in order to show the synthetic interest of acac complexes of different elements.

2. The 'acac method'

It is well-known that the acac ligand usually occupies one or two coordination sites [1,2]. Three-coordination is known but rare [1,2,5,6]. From a synthetic point of view, the reaction of an acac complex with a protic acid AH or BH^+X^- enables the coordination of its conjugate base, A^-, or B, or in the latter case, even both B and X^-, in the coordination position(s) previously occupied by the acac ligand.

$$[\{M\}(acac)] + AH \rightarrow [\{M\}A] + Hacac$$

$$[\{M\}(acac)] + (BH)^+X^- \rightarrow [\{M\}B]X + Hacac$$

$$[\{M\}(acac)] + (BH)^+X^- \rightarrow [\{M\}(B)(X)] + Hacac$$

The by-product, acetylacetone, can be easily separated from the reaction product. However, sometimes the presence of acetylacetone in the reaction mixture induces the formation of oily products when the solvent is removed. In those cases, prolonged stirring of the oil with diethyl ether or with a mixture of diethyl ether and a small amount of acetone usually helps to convert the oil into a solid.

Protonation of the ligand acac and replacement of the weak ligand acetylacetone by the stronger nucleophile A^-, or B, or B and X^- are, reasonably, the key steps in these reactions.

3. Synthesis of gold(III) complexes

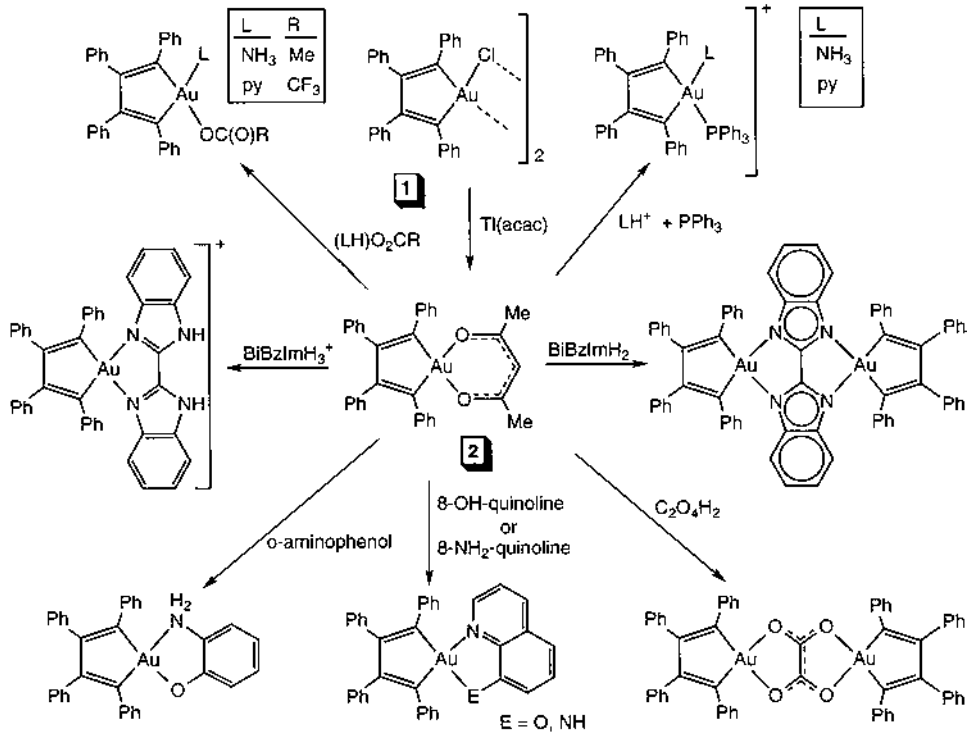
3.1. Auracyclic complexes

The reaction between the auracyclopentadiene **1** and Tl(acac) gave the acetylacetonatogold(III) complex **2** (Scheme 1). On treating **2** with protic acids, neutral or cationic, mono or dinuclear gold(III) complexes were obtained in high yields [7,8]. Thus, reactions of **2** with protonated ligands such as $(BiBzImH_3)ClO_4$ or (LH)X ($L = NH_3$, $X = ClO_4$; L = py, $X = BF_4$) in the presence of PPh_3, gave mononuclear cationic complexes while neutral dinuclear complexes with diprotic tetradentate ligands, $BiBzImH_2$ or oxalic acid were formed. Neutral mononuclear complexes can be prepared by reacting **2** with monoprotic bidentate ligands like 8-hydroxyquino-

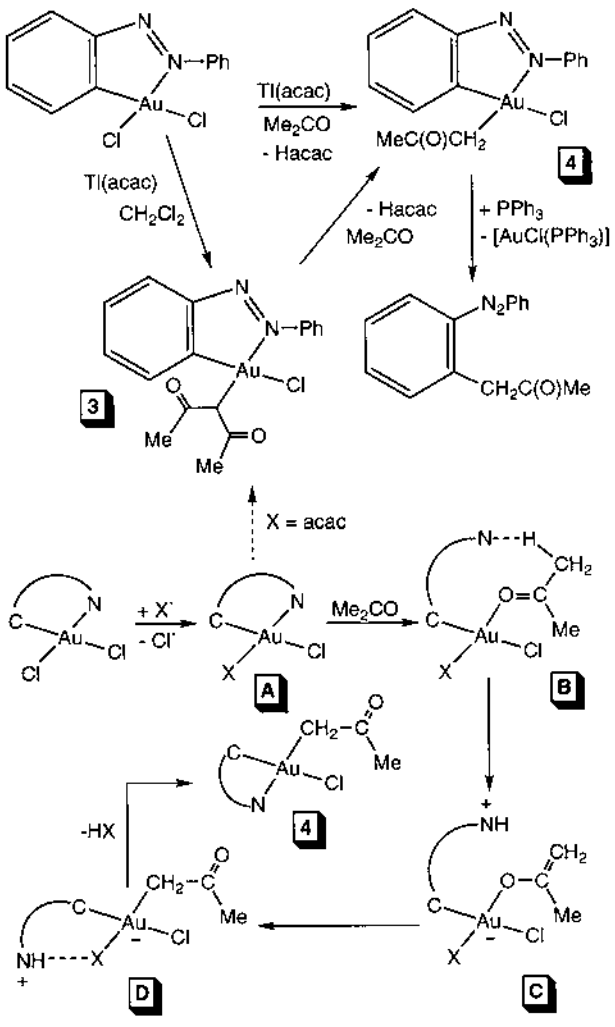
line, 8-aminoquinoline or 2-aminophenol, or with ammonium acetate or pyridinium trifluoroacetate (Scheme 1). These reactions were the first applications of an acac complex in the synthesis of gold complexes.

Similar reactions have been employed to prepare mono, homo and hetero di, tri and tetranuclear Rh, Ir and Ru complexes by reacting $[M(acac)L_2]$ (M = Rh, L = CO, COD, nbd, tfb; M = Ir, L = cod, tfb) and $[Ru(\eta^6\text{-}p\text{-cymene})(acac)L]^{n+}$ ($n = 0$, L = Cl; $n = 1$, L = PPh_3) with O-, N- and S-donor ligands containing acidic hydrogen atoms [9–38]. Likewise, by reacting $[Pd(C_6F_5)_2(acac)]^-$ or $[Pd(C_6X_5)(acac)(PPh_3)]$ (X = F, Cl) with LH_2 (LH_2 = $BiBzImH_2$, 2,2′-biimidazol, tetramethylbiimidazol) dinuclear complexes containing the bridging ligands L^{2-} were obtained [39]. The hexanuclear $[\{(dppm)Au_2(\mu\text{-}BiBzIm)Pd\}_2(\mu\text{-}BiBzIm)]^{2+}$ was obtained by reacting $[(dppm)Au_2(\mu\text{-}BiBzIm)Pd(acac)]^+$ with $H_2BiBzIm$ [40].

Complexes $[Au(C_6F_5)_2(acac)]$, $[Pd(C_6F_5)(acac)(PR_3)]$ and $[Pd(acac)_2]$ react with $(Ph_2P)_3CH$ giving $[Au(C_6F_5)_2\{(Ph_2P)_2C(PPh_2)\}]$ [41], $[Pd(C_6F_5)\{(PPh_2)_2C(PPh_2)\}(PR_3)]$ [42] or $[Pd\{(PPh_2)_2C(PPh_2)\}_2]$ [43], respectively, in which the deprotonated phosphine is coordinated as a κ^2-*P*,*P* chelating ligand. Similarly, $[M(acac)_2]$ and dppm reacted to give $[M\{(PPh_2)_2CH\}_2]$ (M = Pd, Pt) [44].



Scheme 1.



Scheme 2.

3.2. Ketonyl[2-(phenylazo)phenyl]gold(III) complexes

In the development of the chemistry of the orthometallated 2-(phenylazo)phenylgold(III) complexes, we found, fortuitously, that when some substitution reactions were attempted metallation of acetone occurred. Thus, when we tried to prepare [Au(C,N′–C_6H_4N=NPh-2)(C-acac)Cl] (**3**) by reaction of [Au(C,N′–C_6H_4N=NPh-2)Cl_2] with Tl(acac) (1:1) in acetone at room temperature we isolated, instead, [Au(C,N′–C_6H_4N=NPh-2){CH_2C(O)Me}Cl] (**4**) [45–49]. Scheme 2 shows

the proposed reaction pathway for this metallation reaction. The intermediate complex **A** with X = acac (complex **3**), was isolated when the above reaction was carried out in acetone at 0°C or in dichloromethane. As shown in Scheme 2, **3** reacted with acetone at room temperature to give **4**. Similarly, complexes **A** with $X = C_6F_5$ or $C_6H_4NO_2$-2 were obtained by reacting [Au(C,N′–C_6H_4N=NPh-2)Cl_2] with HgX_2 and Cl^- (2:1:2) in chloroform while the same reaction carried out in acetone only yielded complex **4** [45–49]. These results suggest that the strong *trans* effect and influence of the carbon donor ligands X = C-acac, C_6F_5 or $C_6H_4NO_2$-2 allow the cleavage of the Au–N bond and coordination of acetone to give **B**. The fact that [Au(C,N′–C_6H_4N=NPh-2)Cl_2] did not react with acetone proves the importance of the labilizing effect of the ligand *trans* to the N atom in the C–H activation process (step **A** → **B**). Additionally, we have shown the Au–N bond to be weaker in [Au(C,N′–C_6H_4N=NPh-2)Cl_2] than in [Au(C,N–$C_6H_4CH_2NMe_2$-2)Cl_2]. In fact, the first complex reacted with neutral ligands to always give the adduct resulting from the Au–N bond cleavage (e.g. with PPh_3 to give [Au(C_6H_4N=NPh-2)Cl_2(PPh_3)]), while all attempts to cleave the Au–N bond in the second one failed (e.g. with PPh_3 the complex [Au(C,N–$C_6H_4CH_2NMe_2$-2)Cl(PPh_3)]Cl was obtained) [50–57]. Therefore, the observation that complexes [Au(C,N–$C_6H_4CH_2NMe_2$-2)(R)Cl] (R = C-acac, C_6F_5 or $C_6H_4NO_2$-2) can be obtained from [Au(C,N–$C_6H_4CH_2NMe_2$-2)Cl_2] and are stable in acetone solution [58,59], emphasized the influence of the strength of the Au–N bond on the reactivity of these cyclometallated complexes in acetone and supported the proposed step **A** → **B** in the suggested pathway. The step **B** → **C** is similar to that proposed to rationalize the activation of acetone by porphyrin complexes [Rh(L)Cl] [60,61]. The process is completed when the azonium cation **D** transfers a proton to the ligand X and chelation is re-established. Reactions of other ketones and 2-(arylazo)arylgold(III) complexes lead to other ketonyl[2-(arylazo)aryl]gold(III) complexes [49] that reacted with PPh_3 to give benzyl-alkyl and -arylketones (Scheme 2) [62].

Related with these C–H activation processes is the orthometallation of benzylamine by [Pd$(acac)_2$] to give [Pd(acac)($C_6H_4CH_2NH_2$-2)] [63].

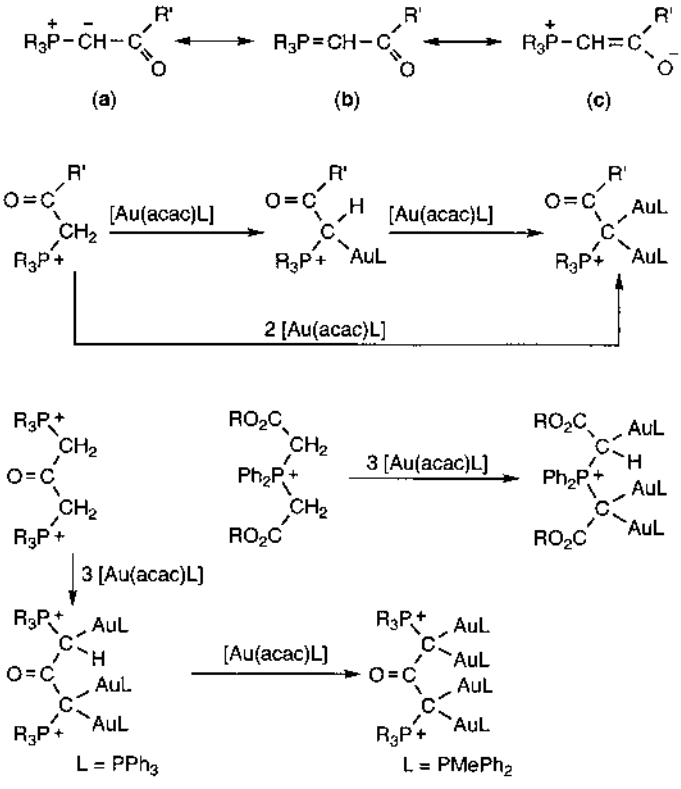
4. Synthesis of gold(I) complexes from [Au(acac)L].

4.1. Complexes with phosphorus ylide ligands

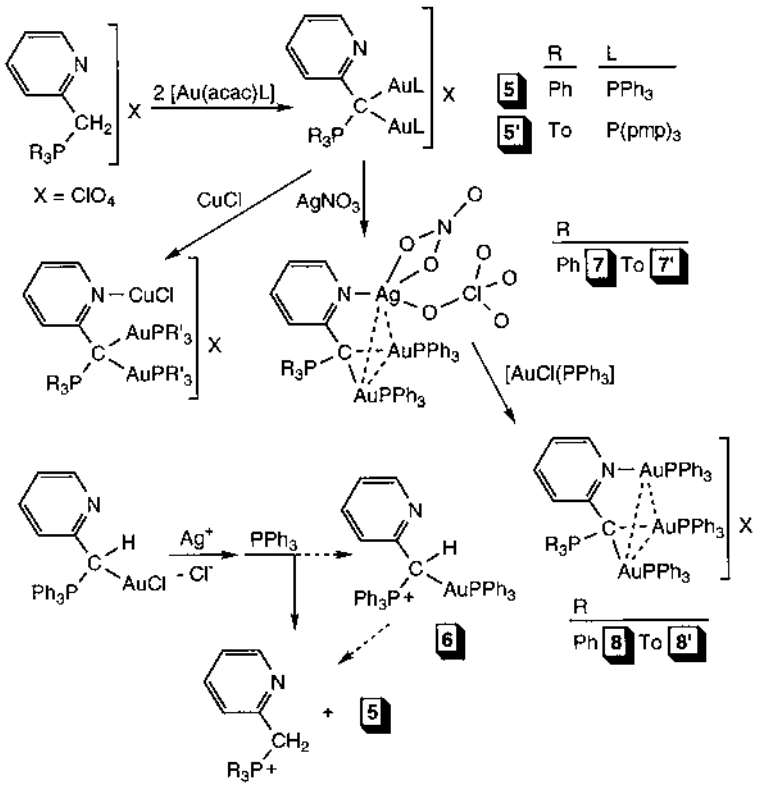
Carbonyl-stabilized phosphorus ylides are weak bases unable to displace ligands readily substituted by non-stabilized ylides. The electronic distribution in phosphorus ylides is described by the two resonance forms (**a**) and (**b**) (Scheme 3). The contribution of a third resonance form (**c**) in β-carbonyl ylides, explains the lower ability to coordinate through the C atom compared with non-stabilized ylides. Accordingly, the corresponding phosphonium salts are more acidic than those derived from non-stabilized ylides. We have taken advantage of the enhanced acidic character of these phosphonium salts to design a new method of synthesis for the

ylide complexes. Thus, by reacting [Au(acac)L] with $[R_3PCH_2C(O)R']ClO_4$ (1:1), complexes $[Au\{CH(PR_3)C(O)R'\}L]ClO_4$ (R = Ph, L = PPh_3, R′ = OMe, OEt [64], Me, Ph [65], NMe_2 [66]; R = OEt, L = $AsPh_3$ [64]) could be isolated (Scheme 3). Although substitution of one H atom by the less electron-withdrawing AuL group decreases the acidity of the remaining H atom [65], it was acidic enough to react with [Au(acac)L] to give dinuclear complexes $[(AuL)_2\{\mu\text{-}C(PR_3)C(O)R'\}]ClO_4$ [R = Ph, L = PPh_3, R′ = OMe, OEt [64], Me, Ph [65], C_6H_4X-4 (X = OMe, NO_2) [67], NMe_2 [66], CN [67]; R′ = OEt, L = $AsPh_3$ [64]). These complexes were also obtained by reacting the phosphonium salt with [Au(acac)L] in molar ratio 1:2 (Scheme 3). A similar reaction between $[Ag\{CH(PPh_3)CO_2R\}_2]ClO_4$ and [Au(acac)L] (1:2) lead to the trinuclear complex $[Ag\{C(PPh_3)(CO_2R)(AuL)\}_2]ClO_4$ [68].

We have extended this method to prepare tri and tetranuclear gold(I) ylide complexes from phosphonium salts containing two α methylene groups. Thus, reactions between $[R_3PCH_2C(O)CH_2PR_3](ClO_4)_2$ and [Au(acac)L] (1:4 molar ratio) gave the trinuclear $[(AuL)_2\{\mu\text{-}C(PR_3)C(O)CH(PR_3)(AuL)\}](ClO_4)_2$ (R = Ph, L = PPh_3) or the tetranuclear $[(AuL)_4\{\mu_4\text{-}\{C(PR_3)\}_2C(O)](ClO_4)_2$ (R = Ph, L = $PPhMe_2$) (Scheme 3) [69]. It is probable that steric hindrance prevents the tetrasubstitution



Scheme 3.



Scheme 4.

when $L = PPh_3$ because it is attained with the less bulky phosphine $PPhMe_2$. Such hindrance is greater in the phosphonium salts $[Ph_2P(CH_2CO_2R)]ClO_4$ because when they reacted with [Au(acac)L] only trinuclear complexes $[(AuL)_2\{\mu\text{-}C(CO_2R)PPh_2CH(AuL)(CO_2R)\}]ClO_4$ ($L = PPh_3$, $R = Me$, Et; $L = PPhMe_2$, $R = Me$; $L = P(pmp)_3$, $R = Et$) were obtained (even when four equivalents of [Au(acac)L] and the smaller $PPhMe_2$ were used). This could be attributed to the different hybridization of the central atom in these phosphonium salts ($C(sp^2)$ and $P(sp^3)$, respectively). Additionally, the double charge of the trinuclear complexes $[(AuL)_2\{\mu\text{-}C(PPh_3)C(O)CH(PPh_3)(AuL)\}]^{2+}$ could account for the enhanced acidity of the last proton while the single charge of the trinuclear $[(AuL)_2\{\mu\text{-}C(CO_2R)PPh_2CH(AuL)(CO_2R)\}]^{+}$ may not be enough.

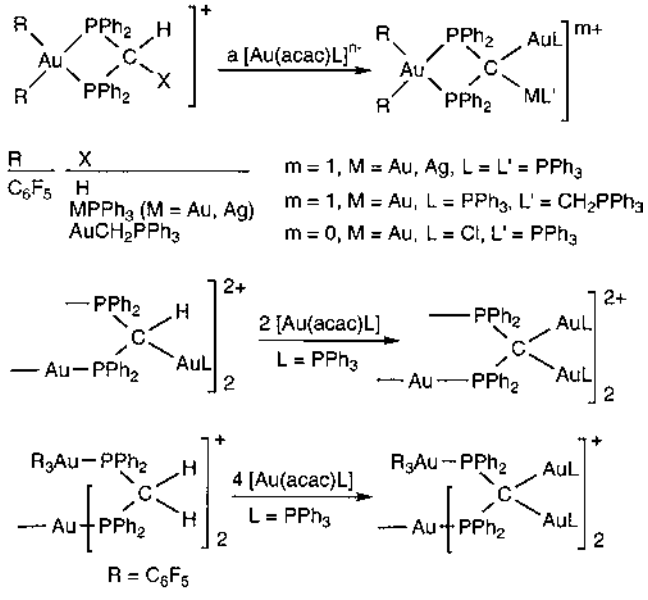
Complexes $[(AuL)_2\{\mu\text{-}C(PR_3)(py\text{-}2)\}]ClO_4$ ($R = Ph$, $L = PPh_3$ (**5**); $R = To$, $L = PPh_3$, $P(pmp)_3$ (**5′**), $P(Cy)_3$, PMe_3) were obtained (Scheme 4) [67,70,71] when phosphonium salts $[R_3PCH_2(py\text{-}2)]ClO_4$ reacted with [Au(acac)L] in a 1:3 molar ratio. If a 1:1 or 1:2 molar ratio is used, mixtures containing **5** (by NMR), the starting materials and a product that could be the mononuclear complex $[Au\{CH(PPh_3)(py\text{-}2)\}(PPh_3)]ClO_4$ (**6**) were obtained. In an attempt to prepare this

complex, we reacted [AuCl{CH(PR_3)(py-2)}] first with $AgClO_4$ and, after removing AgCl, with PPh_3. The isolation of the dinuclear complex **5** and the corresponding phosphonium salt proved that the mononuclear complex disproportionated to these compounds preventing its isolation (Scheme 4). Complex **5** or **5′** reacted with CuCl or $AgNO_3$ to give $[(AuL)_2\{\mu\text{-}C(PR_3)(py\text{-}2)(CuCl)\}]ClO_4$ (L = PPh_3, R = Ph; L = $P(pmp)_3$, R = To] or $[(AuL)_2\{\mu\text{-}C(PR_3)(py\text{-}2)\}\{Ag(O_2NO)(OClO_3)\}]$ (L = PPh_3, R = Ph (**7**)), respectively. Complex **7** reacted with [AuCl(PPh_3)] to form $[(AuL)_2\{\mu\text{-}C(PPh_3)(py\text{-}2)\}(AuPPh_3)]$ (**8**) (Scheme 4).

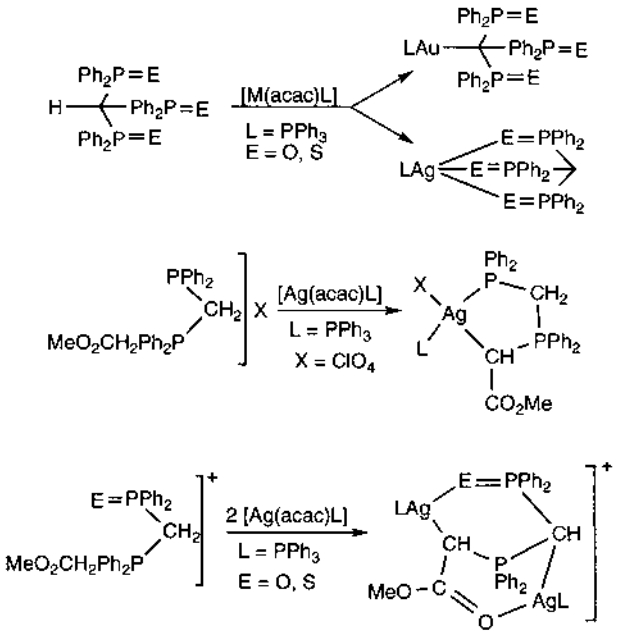
A variable-temperature ^{1}H-NMR study on complexes $[(AuL)_2\{\mu\text{-}C(PTo_3)R\}]ClO_4$ (R = C(O)R′ (R′ = NMe_2, C_6H_4X-4 (X = H, OMe, NO_2), L = PPh_3; R = py-2, L = PR'_3 (R′ = Ph, pmp, $P(Cy)_3$, PMe_3)), **7′** and **8′**, showed that, at room or lower temperatures, the rotation of PTo_3 around the C–P bond is restricted. Although this behaviour can be mainly attributed to steric effects, the concurrence of minor electronic effects cannot be neglected [67].

4.2. Methanide and methanediide complexes

Laguna et al. have studied reactions of [Au(acac)(PPh_3)] with gold(I) and (III) complexes containing $(PPh_2)_2CH_2$ or $SPPh_2CH_2PPh_2$ or $(SPPh_2)_2CH_2$ or related ligands leading to complexes that result from the substitution of one or both methylenic hydrogen atoms of the phosphine by one or two $AuPPh_3$ groups (Scheme 5) [72–75]. By reacting the tetranuclear $[Au_2\{\mu-(PPh_2)_2CH\text{-}(AuPPh_3)\}_2]^{2+}$ or the trinuclear $[\{Au(C_6F_5)_3(\mu-PPh_2CH_2PPh_2)\}_2Au]^+$ with



Scheme 5.



Scheme 6.

$[Au(acac)(PPh_3)]$ the hexanuclear complex $[Au_2\{\mu-(PPh_2)_2C(AuPPh_3)_2\}_2]^{2+}$ [74] or the heptanuclear complex $[\{Au(C_6F_5)_3\{\mu-PPh_2C(AuPPh_3)_2PPh_2\}_2Au]^+$ was obtained [76]. Similarly, complexes $[M(acac)(PPh_3)]$ (Ag or Au) reacted with phosphorus compounds like $[Ph_2P(E)CH_2(PPh_2R)]ClO_4$ (E = electron pair, R = CH_2CO_2Me; E = S or O, R = Me, CH_2Ph or CH_2CO_2Me), $CH\{PPh_2(E)\}_3$ (E = O, S), $(EPPh_2)_2X$ (X = CH_2, NH, E = electron pair, S) (Scheme 6) to give complexes that result from substitution of one or two of the methylenic protons of CH_2P_2 or CH_2CO_2Me (or of both groups) or the proton in the CHP_3 or NH groups by 12 $M(PPh_3)$ [77–80]. The complex $[Au_2\{\mu-(PPh_2)_2CH\{Au(acac)\}\}_2]$ reacted with $[Au(C_6F_5)_2\{(PPh_2)_2CH_2\})]$ (1:2) as expected for an acac complex to give a hexanuclear gold(I)/gold(III) complex [81]. However, $[Mo(CO)_4\{(Ph_2PCH_2)_2C(Me)$-$CH_2P\{Au(acac)\}Ph_2\}]$ deprotonates complexes $[Au(C_6F_5)_3(PPh_2CH_2PPh_2)]$ or $[Mo(CO)_4\{(Ph_2P)_2CHPPh_2\}]$ but the gold atom bonded to the uncoordinated P atom [82]. Similar reactions have been studied using palladium and platinum acac complexes. Thus, the reactions between $[M(C_6X_5)(acac)(L)]$ and dppm gave $[M(C_6X_5)\{(PPh_2)_2CH\}(L)]$ (M = Pd, X = F, L = PR_3; M = Pd, X = Cl, L = dppm; M = Pt, X = F, L = dppm) [83].

4.3. Synthesis of gold(I) complexes with sulfur ylide ligands

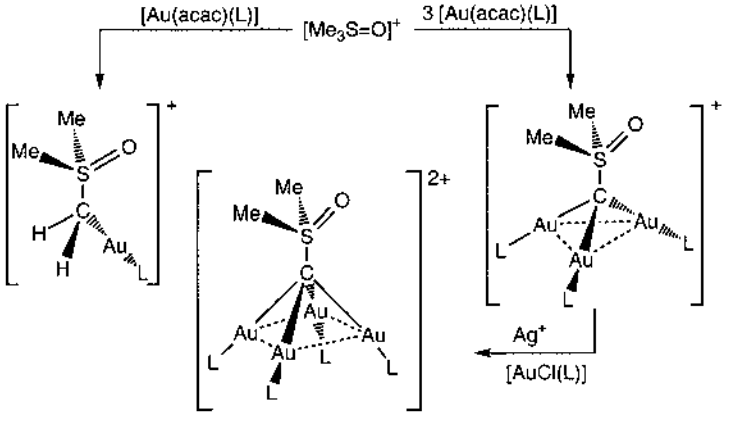
The scarcity of gold complexes with sulfur ylide ligands [84–86] contrasts with the abundancy of those with their phosphorus homologues [67,71,87–94]. We have

prepared mononuclear $[Au\{CH_2S(=O)Me_2\}(PPh_3)]ClO_4$ and trinuclear $[(AuPPh_3)_3\{\mu_3\text{-}CS(=O)Me_2\}]ClO_4$ (**11**) complexes with sulfur ylide ligands by reacting $[Au(acac)(PPh_3)]$ with $[Me_3S{=}O]ClO_4$ in 1:1 and 1:4 molar ratios respectively (Scheme 7) [95]. The 2:1 reaction, intended to produce the dinuclear complex $[(AuPPh_3)_2\{\mu\text{-}CHS(=O)Me_2\}]ClO_4$ gave, the 1:1 and 1:3 products also and the mixture could not be resolved. The reaction of **11** with $AgClO_4$ and $[AuCl(PPh_3)]$ produced the hypercoordinate complex $[(AuPPh_3)_4\{\mu_4\text{-}CS(=O)Me_2\}](ClO_4)_2$, the crystal structure of which shows the ylide carbon atom in a square pyramidal environment with an apical $S(=O)Me_2$ group and four basal $AuPPh_3$ groups (Scheme 7) [95]. It did not react further with $[Au(OCMe_2)(PPh_3)]ClO_4$

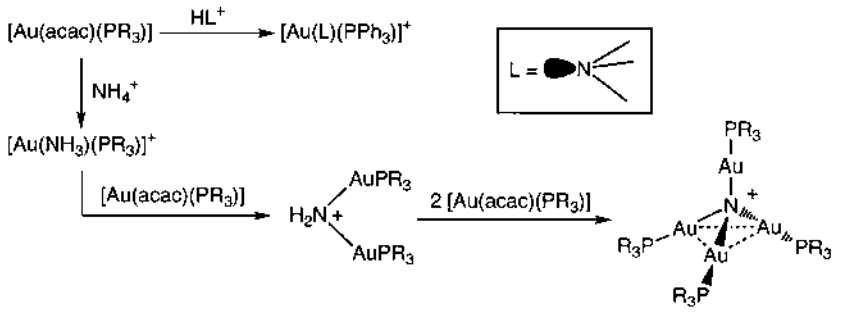
4.4. Gold(I) complexes with N-donor ligands

Gold(I) complexes with neutral N-donor ligands are much less common than those with P-donor ligands due to the soft acid nature of the metal centre. We have extended the use of acac gold(I) complexes to the synthesis of a family of cationic complexes $[Au(L)(PR_3)]X$ ($X = CF_3SO_3$, $L = MeNH_2$, 2- and 4-nitroaniline, 4-methoxyaniline, $NHPh_2$, $NHEt_2$; $X = ClO_4$, $L = NMe_3$] or $[(AuPPh_3)_2\{\mu\text{-}H_2N(CH_2)_2NH_2\}$) by reacting $[Au(acac)(PR_3)]$ with primary, secondary or tertiary ammonium salts [HL]X (1:1) (Scheme 8). The result of these reactions depend on the nature of the solvent. Acetone could only be used in the synthesis of the tertiary amine complex [96,97]. In all other cases, acetone had to be excluded to prevent the formation of iminogold(I) complexes [98].

Reactions of $[Au(acac)(PR_3)]$ ($R = Ph$, pmp) with $(NH_4)ClO_4$ allowed us to synthesize mono-, di- and tetraaurated ammonium salts (Scheme 8). Depending on the reaction conditions the first amminogold(I) complexes $[Au(NH_3)(PR_3)]ClO_4$, or the first imidogold(I) complexes $[(AuPR_3)_2(\mu\text{-}NH_2)]ClO_4$, or nitrido complexes $[(AuPR_3)_4(\mu_4\text{-}N)]ClO_4$ were prepared. Our method for preparing nitridogold(I) complexes is simpler and gives higher yields than those reported previously [99,100].



Scheme 7.



Scheme 8.

5. Synthesis of gold complexes from anionic acac gold(I) complexes

The complex ppn[Au(acac)$_2$] (**9**) was prepared by reacting ppn[AuCl$_2$] with Tl(acac) in 1:2 molar ratio (Scheme 9) [101,102]. An alternative route was reported by Laguna et al. [72]. The first step of this process involved the reaction of [AuCl(tht)] with ppn(acac) [prepared from Tl(acac) and ppnCl] to give ppn[Au-(acac)Cl]. The reaction of this complex with Tl(acac) in 1:1 molar ratio leads to **9**. The synthesis of Bu_4N[Au(acac)$_2$] was also reported using the same two-steps procedure [76].

A preliminary communication showed the synthetic utility of **9** by reacting it with compounds containing acidic CH, SH or PH groups. Thus, the reaction of **9** with XH or YH^+, in a 1:2 molar ratio, gave anionic ppn[AuX$_2$] (X = RR′CH (R = R′ = CN, CO_2Me; R = CN, R′ = CO_2Me), $Me_3SiC{\equiv}C$ or (py-2)S) or cationic $[AuY_2]^+$ (Y = CH(PTo_3)(py-2)) complexes, respectively [101].

5.1. Synthesis of gold(I) complexes with P-donor ligands

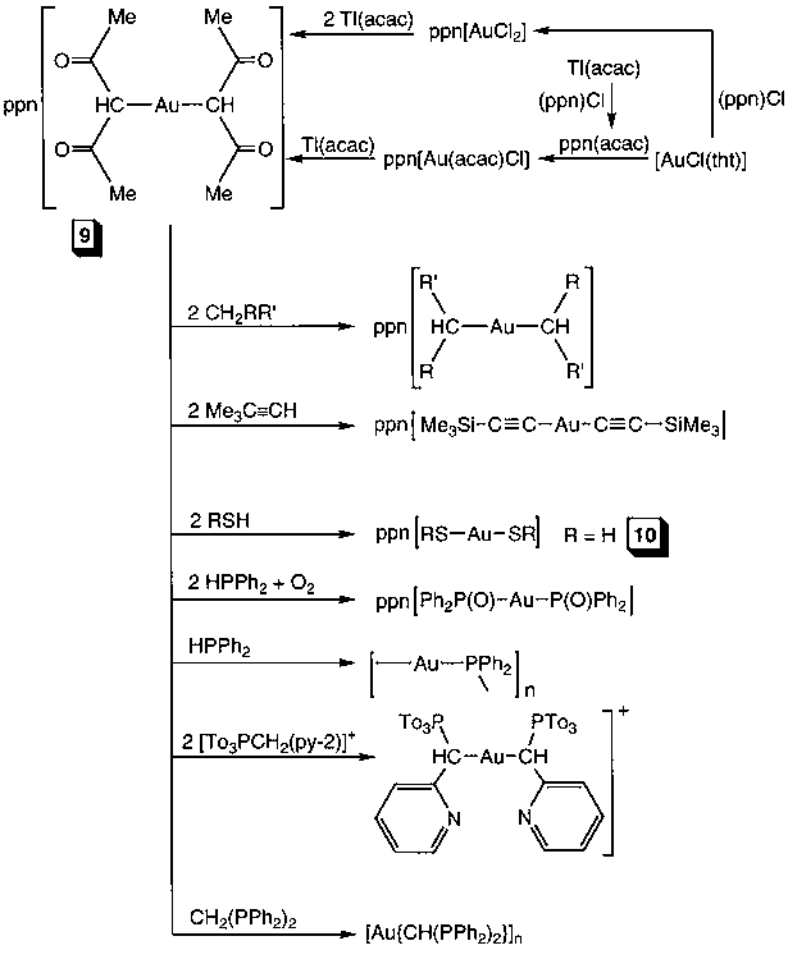
The reaction of **9** with $HPPh_2$, in a 1:1 molar ratio, led to the neutral polymeric compound $[Au(PPh_2)]_n$ (Scheme 9) which was also obtained by reacting [Au-(acac)(PPh_3)] with Ph_2PH in a 1:1 molar ratio [101]. The reaction of **9** with Ph_2PH, in the molar ratio 1:2, gave the complex, ppn[Au{P(O)Ph_2}$_2$], as a result of the aerial oxidation of the expected complex ppn[Au(PPh_2)$_2$] (Scheme 9) [103].

Diphenylphosphido bridged $[L_mMn_n(\mu\text{-}PPh_2)_pAu_xX_y]^z$ complexes ($L_m = (CO)_5$, bipy$(CO)_3$, X = PR_3, $n = p = x = y = z = 1$; $L_m = (CO)_4$, $n = 1$, $p = x = y = 2$, X = PR_3, $z = 1$, X = C_6F_5, $z = -1$; $L_m = (CO)_5$, bipy$(CO)_3$, $n = p = 2$, $x = z = 1$, $y = 0$; $L_m = (CO)_8$, $n = x = 2$, $p = 4$, $y = z = 0$) have been prepared by reacting complexes $[L_mMn_n(PHPh_2)_p]A$ ($p = 1$, 2, A = ClO_4, PF_6) with [AuCl(L)] (L = PR_3, tht) or [Au(C_6F_5)(tht)] in the presence of appropiate proportions of K(acac), Tl(acac) or ppn(acac) [104]. Similarly, $HPPh_2$ and $HP(S)Ph_2$ reacted with [M(C_6F_5)(acac)L] to give [Pd(C_6F_5)(μ-PPh_2)(PPh_2H)]$_2$ and [Pd(C_6F_5){P(S)Ph_2}L_2] (L_2 = phen, bipy) or [M(C_6F_5){μ-P(S)Ph_2}L]$_2$ (M = Pd, Pt; L = PR_3), respectively [105,106]. Complexes [M{P(S)Ph_2}(PPh_3)$_2$]$^+$ were obtained by reacting [M(acac)(PPh_3)$_2$]$^+$ with $HP(S)Ph_2$ (M = Pd, Pt) [106].

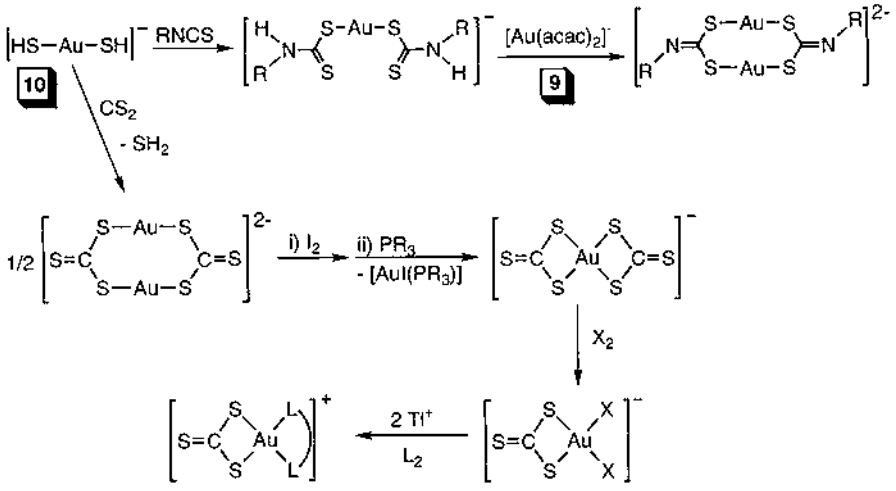
5.2. Synthesis of gold(I) complexes with sulfur donor ligands

Interest in complexes containing Au–S bonds stems mainly from their potential applications in medicine (chrysotherapy). The reported yields of the few previously described anionic thiolatogold(I) complexes $[Au(SR)_2]^-$ were low (35–38%) [107–109]. The reaction of **9** with thiols RSH in a 1:2 molar ratio resulted in preparation of a family of anionic thiolato gold(I) complexes ppn$[Au(SR)_2]$ (RSH = benzoxazole-2(1*H*)-thione, pyrimidine-2(1*H*)-thione, pyridine-2(1*H*)-thione, 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranose, 2-thiouracyl(2,3-dihydro-2-sulfanylethanol, 2,3-dihydro-1*H*-benzimidazole-2-thione, 2-thiomalic acid, 2-sulfanylethanol, D-penicillamine) in high yields (Scheme 9) [110].

Although it has been suggested that considerable quantities of gold may be transported in hydrothermal ore solutions as $[Au(SH)_2]^-$, it had never been



Scheme 9.



Scheme 10.

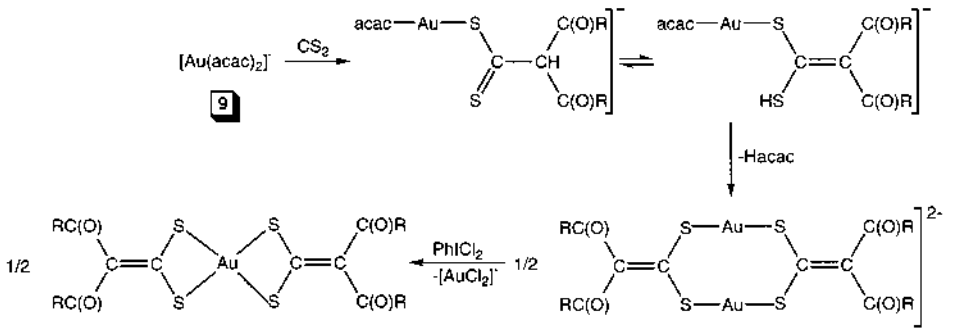
isolated. The ppn salt of this anion, **10**, was obtained (91% yield) by slow addition of a solution of **9** to a saturated solution of H_2S, both in CH_2Cl_2 (Scheme 9). Complex **10** is the first isolated homoleptic hydrogensulfide metal complex [111]. A family of trithiocarbonatogold complexes has its origin in the reaction between **10** and CS_2 which gave the first trithiocarbonatogold complex: $ppn_2[Au_2(\mu\text{-}\kappa^2\text{-}CS_3)_2]$ (Scheme 10) [112]. Iodine oxidation of this complex and subsequent addition of PR_3 allowed the isolation of the trithiocarbonatogold(III) complex $ppn[Au(CS_3)_2]$ which reacted with $PhICl_2$ or I_2 to give $ppn[Au(CS_3)X_2]$ (X = Cl, I). Finally, the latter complex (X = Cl) reacted with L_2 (phen, bipy) and TlO_3SCF_3 to give cationic complexes $[Au(CS_3)L_2](O_3SCF_3)$ (Scheme 10) [113].

The reaction of **10** with isothiocyanates RNCS containing strong electron withdrawing R groups ($C_6H_4NO_2$-4, C_6F_5) gave monosubstituted dithiocarbamato complexes $ppn[Au\{SC(=S)NHR\}_2]$ that reacted with **9** to give the first dinuclear dithiocarbimato complexes of the type $ppn_2[Au_2(\mu\text{-}k^2\text{-}S_2C{=}NR)_2]$ in almost quantitative yields (Scheme 10) [114].

β-Diketonato complexes $ppn[Au\{CH(COR)_2\}_2]$ (R = Me (**9**), Ph) reacted with CS_2 to give complexes $ppn_2[Au_2\{\mu\text{-}k^2\text{-}S_2C{=}C(COR)_2\}_2]$. Although this is an insertion reaction, an intermediate acid–base reaction giving acetylacetone must occur (Scheme 11) [115]. These are the first fully characterized 2,2-diacylethylene-1,1-dithiolato complexes of any element.

5.3. Synthesis of alkynyl gold(I) complexes

We have reported the synthesis of the first family of ethynylgold(I) complexes by reacting **9** with acetylene to give $ppn[Au(C{\equiv}CH)_2]$ and reacting this complex with $ppn[AuX_2]$ or $[Au(PR_3)_2]ClO_4$ to give $ppn[AuX(C{\equiv}CH)]$ (X = Cl, Br, I) or

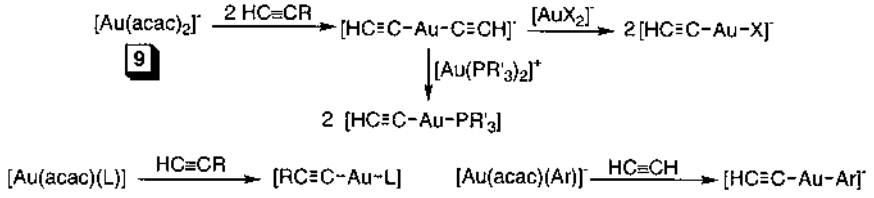


Scheme 11.

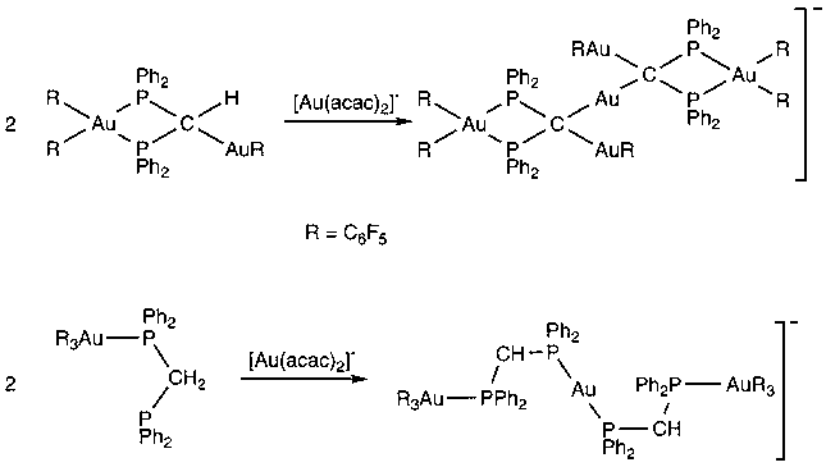
$[Au(C{\equiv}CH)(PR_3)]$ (R = Ph, pmp), respectively (Scheme 12). Similarly, **9** reacted with different alkynes to give ppn$[Au(C{\equiv}CR)_2]$ [R = Bu^t, $SiMe_3$, CH_2X (X = Cl, Br, OH), $C_6H_4NO_2$-4, $C_6H_4C{\equiv}CH$-4, $C_6H_4C_6H_4NO_2$-4,4′, $C_6H_4CH=CHC_6H_4NO_2$-4,4′-E] [116–118]. By reacting $[AuCl\{C(NH^tBu)(NEt_2)\}]$ with Tl(acac), a new acac complex $[Au(acac)\{C(NH^tBu)(NEt_2)\}]$ could be obtained. This complex or [Au(acac)L] reacted with terminal alkynes to form $[Au(C{\equiv}CR)(L)]$ [R = H, ^{t}Bu, $SiMe_3$, L = $C(NH^tBu)(NEt_2)$, PPh_3, $P(pmp)_3$; R = CH_2X (X = Cl, Br, OH), L = PCy_3] (Scheme 12) [116,118]. The first ethynyl(aryl)aurate(I) complexes, ppn$[Au(C{\equiv}CH)(Ar)]$ [Ar = C_6F_5, $C_6H_4NO_2$-2, $C_6H_2(NO_2)_3$-2,4,6], have been obtained by treating the corresponding ppn[AuCl(Ar)] complexes with Tl(acac), removing TlCl, and bubbling acetylene through the resulting solution. It is reasonable to assume that, in a first step, ppn[Au(acac)(R)] complexes were formed, but we have not been able to isolate them because of their low stability [118].

5.4. Methanide and methanediide gold(I) and gold(III) complexes

Complex **9** reacted with dppm to give the polymeric complex $[Au\{CH(PPh_2)_2\}]_n$ (Scheme 9) [101]. Similarly, $[Au(C_6F_5)_2\{(PPh_2)_2CH(ML)\}]^n$ reacted with ppn[Au(acac)Cl] (1:1) or **9** (2:1) to give $[Au(C_6F_5)_2\{(PPh_2)_2C(AuCl)(ML)\}]^n$ ($n = 0$, M = Au, L = PPh_3, CH_2PPh_3, M = Ag, L = PPh_3; $n = -1$, M = Au, L = C_6F_5) or $[Au(C_6F_5)_2\{(PPh_2)_2C(ML)\}_2Au]^{1-}$ (M = Au, L = C_6F_5) (Scheme 13), respectively [72]. Related reactions of $[Au(C_6F_5)_3(PPh_2CH_2PPh_2)]$ or $[M(CO)_4\{(PPh_2)_2CHPPh_2\}]$ (M = Cr, Mo, W) with $Bu_4N[Au(acac)_2]$ afforded $[\{Au(C_6F_5)_3(\mu-PPh_2CHPPh_2)\}_2Au]^-$ [76] (Scheme 13) or $[M(CO)_4\{\mu\text{-}(PPh_2)_2CPPh_2\}_2Au]^-$ [119].



Scheme 12.



Scheme 13.

6. Conclusion

In this review we have shown the synthetic utility of acac gold complexes in synthesis. Similar reactions were proved successful in the chemistry of other elements. Since acac complexes of most metallic elements are known, stable and easy to prepare, we believe that the 'acac method' could be used to easily prepare coordination and organometallic complexes of most elements.

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References

[1] R.C. Mehrotra, R. Bohra, D.P. Gaur, Metal β-Diketonates and Allied Derivatives, Academic Press, London, 1978.
[2] D. Gibson, Coord. Chem. Rev. 4 (1969) 225.
[3] T. Ito, A. Yamamoto, J. Organomet. Chem. 161 (1978) 61.
[4] T. Ito, A. Yamamoto, J. Organomet. Chem. 174 (1979) 237.
[5] J. Forniés, R. Navarro, M. Tomas, E.P. Urriolabeitia, Organometallics 12 (1993) 940.
[6] J. Forniés, F. Martinez, R. Navarro, E.P. Urriolabeitia, Organometallics 15 (1996) 1813.
[7] M.T. Chicote, Ph.D. thesis, University of Zaragoza, July 1980.
[8] R. Usón, J. Vicente, M.T. Chicote, J. Organomet. Chem. 209 (1981) 271.
[9] L.A. Oro, M.J. Fernández, J. Modrego, J.M. López, J. Organomet. Chem. 287 (1985) 409.
[10] L.A. Oro, M.J. Fernández, J. Modrego, C. Foces-Foces, F.H. Cano, Angew. Chem. Int. Ed. Engl. 23 (1984) 913.

[11] M.A. Calvo, A.M.M. Lanfredi, L.A. Oro, M.T. Pinillos, C. Tejel, A. Tripicchio, F. Ugozzoli, Inorg. Chem. 32 (1993) 1147.
[12] L.A. Oro, M.A. Ciriano, B.E. Villarroya, A. Tiripicchio, F.J. Lahoz, J. Chem. Soc. Chem. Commun. (1984) 521.
[13] C. Tejel, B.E. Villarroya, M.A. Ciriano, L.A. Oro, M. Lanfranchi, A. Tiripicchio, M. Tiripicchio-Camellin, Inorg. Chem. 35 (1996) 4360.
[14] L.A. Oro, M.T. Pinillos, C. Tejel, C. Foces-Foces, F.H. Cano, J. Chem. Soc. Chem. Commun. (1984) 1687.
[15] R. Usón, L.A. Oro, J. Gimeno, M.A. Ciriano, J.A. Cabeza, A. Tiripicchio, M. Tiripicchio-Camellini, J. Chem. Soc. Dalton Trans. (1983) 323.
[16] L.A. Oro, D. Carmona, M.P. Lamata, A. Tiripicchio, F.J. Lahoz, J. Chem. Soc. Dalton Trans. (1986) 15.
[17] L.A. Oro, D. Carmona, J. Reyes, C. Foces-Foces, F.H. Cano, J. Chem. Soc. Dalton Trans. (1986) 31.
[18] L.A. Oro, M.T. Pinillos, C. Tejel, C. Foces-Foces, F.H. Cano, J. Chem. Soc. Dalton Trans. (1986) 1087.
[19] L.A. Oro, M.T. Pinillos, C. Tejel, M.C. Apreda, C. Foces-Foces, F.H. Cano, J. Chem. Soc. Dalton Trans. (1988) 1927.
[20] M.T. Pinillos, C. Tejel, L.A. Oro, M.C. Apreda, C. Foces-Foces, F.H. Cano, J. Chem. Soc. Dalton Trans. (1989) 1133.
[21] M.T. Pinillos, A. Elduque, L.A. Oro, F.J. Lahoz, F. Bonati, A. Tiripicchio, M. Tiripicchio-Camellini, J. Chem. Soc. Dalton Trans. (1990) 989.
[22] D. Carmona, J. Ferrer, F.J. Lahoz, L.A. Oro, J. Reyes, M. Esteban, J. Chem. Soc. Dalton Trans. (1991) 2811.
[23] R. Usón, L.A. Oro, M.A. Ciriano, M.T. Pinillos, A. Tiripicchio, M.T. Camellini, J. Organomet. Chem. 205 (1981) 247.
[24] A. Tiripicchio, M.T. Camellini, R. Usón, L.A. Oro, M.A. Ciriano, M.T. Pinillos, J. Organomet. Chem. 224 (1982) 207.
[25] R. Usón, L.A. Oro, M.A. Ciriano, M.C. Bello, J. Organomet. Chem. 240 (1982) 199.
[26] L.A. Oro, D. Carmona, M.P. García, F.J. Lahoz, J. Reyes, F.H. Cano, C. Foces-Foces, J. Organomet. Chem. 296 (1985) C43.
[27] M.T. Pinillos, A. Elduque, L.A. Oro, J. Organomet. Chem. 338 (1987) 411.
[28] D. Carmona, J. Ferrer, R. Atencio, F.J. Lahoz, L.A. Oro, M.P. Lamata, Organometallics 14 (1995) 2057.
[29] P. Cornago, C. Escolástico, M.D.S. María, R.M. Claramunt, D. Carmona, M. Esteban, L.A. Oro, C. Foces-Foces, A.L. Llamas-Saiz, J. Elguero, J. Organometal. Chem. 467 (1994) 293.
[30] M.T. Pinillos, M.P. Jarauta, L.A. Oro, A. Tiripicchio, M. Tiripicchio-Camellini, J. Organomet. Chem. 339 (1988) 181.
[31] L.A. Oro, M.T. Pinillos, M.P. Jarauta, Polyhedron 4 (1985) 325.
[32] A. Elduque, F. Aguilera, F.J. Lahoz, J.A. López, L.A. Oro, M.T. Pinillos, Inorg. Chim. Acta 274 (1998) 15.
[33] M.T. Pinillos, A. Elduque, E. Berkovich, L.A. Oro, J. Organomet. Chem. 509 (1996) 89.
[34] A. Elduque, L.A. Oro, M.T. Pinillos, C. Tejel, A. Tiripicchio, F. Ugozzoli, J. Chem. Soc. Dalton Trans. (1991) 2807.
[35] M.T. Pinillos, A. Elduque, E. Martin, N. Navarro, F.J. Lahoz, J.A. Lopez, L.A. Oro, Inorg. Chem. 34 (1995) 111.
[36] D. Carmona, J. Ferrer, A. Mendoza, F. Lahoz, L.A. Oro, F. Viguri, J. Reyes, Organometallics 14 (1995) 2066.
[37] J.J. Perez-Torrente, M.A. Casado, M.A. Ciriano, F.J. Lahoz, L.A. Oro, Inorg. Chem. 35 (1996) 1782.
[38] M.T. Pinillos, R. Dhillon, A. Elduque, L.A. Oro, Rhodium Ex. 5 (1994) 4.
[39] R. Usón, J. Gimeno, J. Forniés, F. Martinez, Inorg. Chim. Acta 50 (1981) 173.
[40] R. Usón, J. Gimeno, J. Forniés, F. Martinez, C. Fernández, Inorg. Chim. Acta 63 (1982) 91.
[41] E.J. Fernández, M.C. Gimeno, P.G. Jones, B. Ahrens, A. Laguna, M. Laguna, J.M.L. De Luzuriaga, J. Chem. Soc. Dalton Trans. (1994) 3487.
[42] J. Forniés, F. Martinez, R. Navarro, E.P. Urriolabeitia, Polyhedron 9 (1990) 2181.
[43] J. Forniés, F. Martinez, R. Navarro, M. Tomas, E.P. Urriolabeitia, J. Chem. Soc. Dalton Trans. (1994) 505.

[44] H. Hashimoto, Y. Nakamura, S. Okeya, Inorg. Chim. Acta 120 (1986) L25.
[45] J. Vicente, M.D. Bermúdez, M.T. Chicote, M.J. Sánchez-Santano, J. Chem. Soc. Chem. Commun. (1989) 141.
[46] J. Vicente, M.D. Bermúdez, M.T. Chicote, M.J. Sánchez-Santano, J. Chem. Soc. Dalton Trans. (1990) 1945.
[47] J. Vicente, M.D. Bermúdez, J. Escribano, M.P. Carrillo, P.G. Jones, J. Chem. Soc. Dalton Trans. (1990) 3083.
[48] J. Vicente, M.D. Bermúdez, M.P. Carrillo, P.G. Jones, J. Chem. Soc. Dalton Trans. (1992) 1975.
[49] J. Vicente, M.D. Bermúdez, M.P. Carrillo, P.G. Jones, J. Organomet. Chem. 456 (1993) 305.
[50] J. Vicente, M.T. Chicote, Inorg. Chim. Acta 54 (1981) L259.
[51] J. Vicente, M.T. Chicote, M.D. Bermúdez, Inorg. Chim. Acta 63 (1982) 35.
[52] J. Vicente, M.T. Chicote, M.D. Bermúdez, J. Organomet. Chem. 268 (1984) 191.
[53] J. Vicente, M.T. Chicote, M.D. Bermúdez, M. García-García, J. Organomet. Chem. 295 (1985) 125.
[54] J. Vicente, M.T. Chicote, M.D. Bermúdez, M.J. Sánchez-Santano, P.G. Jones, C. Fittschen, G.M. Sheldrick, J. Organomet. Chem. 310 (1986) 401.
[55] J. Vicente, M.T. Chicote, M.D. Bermúdez, X. Solans, M. Font-Altaba, J. Chem. Soc. Dalton Trans. (1984) 557.
[56] J. Vicente, M.T. Chicote, M.D. Bermúdez, P.G. Jones, C. Fittschen, G.M. Sheldrick, J. Chem. Soc. Dalton Trans. (1986) 2361.
[57] J. Vicente, M.T. Chicote, M.D. Bermúdez, P.G. Jones, G.M. Sheldrick, J. Chem. Res. S 72 (1985) 954.
[58] J. Vicente, M.D. Bermúdez, M.T. Chicote, M.J. Sánchez-Santano, J. Organomet. Chem. 371 (1989) 129.
[59] J. Vicente, M.D. Bermúdez, M.T. Chicote, M.J. Sánchez-Santano, J. Organomet. Chem. 381 (1990) 285.
[60] Y. Aoyama, A. Yamagishi, Y. Tanaka, H. Toi, H. Ogoshi, J. Am. Chem. Soc. 109 (1987) 4735.
[61] Y. Aoyama, Y. Tanaka, A. Yoshida, H. Toi, H. Ogoshi, J. Organomet. Chem. 329 (1987) 251.
[62] J. Vicente, M.D. Bermúdez, F.J. Carrión, Inorg. Chim. Acta 220 (1994) 1.
[63] S. Baba, S. Kawaguchi, Inorg. Nucl. Chem. Lett. 11 (1975) 415.
[64] J. Vicente, M.T. Chicote, J.A. Cayuelas, J. Fernández-Baeza, P.G. Jones, G.M. Sheldrick, P. Espinet, J. Chem. Soc. Dalton Trans. (1985) 1163.
[65] J. Vicente, M.T. Chicote, I. Saura-Llamas, J. Turpín, J. Fernández-Baeza, J. Organomet. Chem. 333 (1987) 129.
[66] J. Vicente, M.T. Chicote, M.C. Lagunas, P.G. Jones, J. Chem. Soc. Dalton Trans. (1991) 2579.
[67] J. Vicente, M.T. Chicote, M.C. Lagunas, P.G. Jones, B. Ahrens, Inorg. Chem. 36 (1997) 4938.
[68] J. Vicente, M.T. Chicote, J. Fernández-Baeza, J. Martin, I. Saura-Llamas, J. Turpin, J. Organomet. Chem. 331 (1987) 409.
[69] J. Vicente, M.T. Chicote, I. Saura-Llamas, P.G. Jones, K. Meyer-Bäse, C.F. Erdbrügger, Organometallics 7 (1988) 997.
[70] J. Vicente, M.T. Chicote, M.C. Lagunas, P.G. Jones, J. Chem. Soc. Chem. Commun. (1991) 1730.
[71] J. Vicente, M.T. Chicote, M.C. Lagunas, Inorg. Chem. 32 (1993) 3748.
[72] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, J.M. Lopez de Luzuriaga, J. Chem. Soc. Dalton Trans. (1992) 3365.
[73] A. Laguna, M.C. Gimeno, Trends Organomet. Chem. 1 (1994) 231.
[74] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, J.M. Lopez de Luzuriaga, Angew. Chem. Int. Ed. Engl. 33 (1994) 87.
[75] B. Alvarez, E.J. Fernandez, M.C. Gimeno, P.G. Jones, A. Laguna, J.M. Lopez de Luzuriaga, Polyhedron 17 (1998) 2029.
[76] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, J.M. López de Luzuriaga, Organometallics 14 (1995) 2918.
[77] M.C. Gimeno, P.G. Jones, A. Laguna, M.D. Villacampa, J. Chem. Soc. Dalton Trans. (1995) 805.
[78] M.C. Gimeno, P.G. Jones, A. Laguna, M.D. Villacampa, Chem. Ber. 129 (1996) 585.
[79] M.C. Gimeno, A. Laguna, M. Laguna, F. Sanmartin, P.G. Jones, Organometallics 12 (1993) 3984.
[80] M.C. Gimeno, A. Laguna, M. Laguna, F. Sanmartin, P.G. Jones, Organometallics 13 (1994) 1538.
[81] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, J.M. Lopez de Luzuriaga, M.A. Rodriguez, Chem. Ber. 128 (1995) 121.

[82] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, E. Olmos, J. Chem. Soc. Dalton Trans. (1996) 3603.
[83] J. Forniés, R. Navarro, E.P. Urriolabeitia, J. Organomet. Chem. 390 (1990) 257.
[84] Y. Yamamoto, Bull. Chem. Soc. Jpn. 60 (1987) 1189.
[85] I.J.B. Lin, C.W. Liu, L.K. Liu, Y.S. Wen, Organometallics 11 (1992) 1447.
[86] J. Stein, J.P.J. Fackler, C. Paparizos, H.-W. Chen, J. Am. Chem. Soc. 103 (1981) 2192.
[87] W.C. Kaska, Coord. Chem. Rev. 48 (1983) 1.
[88] A.V. Johnson, Ylides and Imines of Phosphorus, Wiley, New York, 1993.
[89] J.P. Fackler Jr., Polyhedron 16 (1997) 1.
[90] J. Vicente, M.T. Chicote, M.C. Lagunas, P.G. Jones, E. Bembenek, Organometallics 13 (1994) 1243.
[91] M. Bardaji, E. Cerrada, P.G. Jones, A. Laguna, M. Laguna, J. Chem. Soc. Dalton Trans. (1997) 2263 and references therein
[92] H. Schmidbaur, Angew. Chem. Int. Ed. Engl. 22 (1983) 907.
[93] H. Schmidbaur, Acc. Chem. Res. 8 (1975) 62.
[94] H. Schmidbaur, Pure Appl. Chem. 50 (1978) 19.
[95] J. Vicente, M.T. Chicote, R. Guerrero, P.G. Jones, J. Am. Chem. Soc. 118 (1996) 699.
[96] J. Vicente, M.T. Chicote, R. Guerrero, P.G. Jones, J. Chem. Soc. Dalton Trans. (1995) 1251.
[97] J. Vicente, M.T. Chicote, R. Guerrero, P.G. Jones, M.C. Ramírez de Arellano, Inorg. Chem. 36 (1997) 4438.
[98] J. Vicente, M.T. Chicote, R. Guerrero, unpublished results.
[99] E.G. Perevalova, E.I. Smyslova, V.P. Djadchenko, K.I. Grandberg, A.N. Nesmeyanov, Izv. Akad Nauk SSSR, Ser. Khim. (1980) 1455; Chem. Abstr. 93 (1980) 178615h.
[100] K. Angermaier, H. Schmidbaur, J. Chem. Soc. Dalton Trans. (1995) 559.
[101] J. Vicente, M.T. Chicote, I. Saura-Llamas, M.C. Lagunas, J. Chem. Soc. Chem. Commun. (1992) 915.
[102] J. Vicente, M.T. Chicote, Inorg. Synth. 32 (1998) 172.
[103] J. Vicente, M.T. Chicote, P.G. Jones, Inorg. Chem. 32 (1993) 4960.
[104] G.A. Carriedo, V. Riera, M.L. Rodríguez, P.G. Jones, J. Lautner, J. Chem. Soc. Dalton Trans. (1989) 639.
[105] J. Forniés, F. Martinez, R. Navarro, E.P. Urriolabeitia, J. Organomet. Chem. 495 (1995) 185.
[106] J. Forniés, F. Martinez, R. Navarro, E.P. Urriolabeitia, A.J. Welch, J. Chem. Soc. Dalton Trans. (1993) 2147.
[107] G.A. Bowmaker, B.C. Dobson, J. Chem. Soc. Dalton Trans. (1981) 267.
[108] P.A. Bates, J.M. Waters, Acta Crystallogr. Sect. C 41 (1985) 862.
[109] W. Beck, K.H. Stetter, S. Tadros, K.E. Schwarzhans, Chem. Ber. 100 (1967) 3944.
[110] J. Vicente, M.T. Chicote, P. González-Herrero, P.G. Jones, J. Chem. Soc. Dalton Trans. (1994) 3183.
[111] J. Vicente, M.T. Chicote, P. González-Herrero, P.G. Jones, B. Ahrens, Angew. Chem. Int. Ed. Engl. 33 (1994) 1852.
[112] J. Vicente, M.T. Chicote, P. González-Herrero, P.G. Jones, J. Chem. Soc. Chem. Commun. (1995) 745.
[113] J. Vicente, M.T. Chicote, P. González-Herrero, P.G. Jones, Inorg. Chem. 36 (1997) 5735.
[114] J. Vicente, M.T. Chicote, P. González-Herrero, unpublished results.
[115] J. Vicente, M.T. Chicote, P. González-Herrero, P.G. Jones, Chem. Commun. (1997) 2047.
[116] J. Vicente, M.T. Chicote, M.D. Abrisqueta, P.G. Jones, Organometallics 16 (1997) 5628.
[117] J. Vicente, M.T. Chicote, M.D. Abrisqueta, J. Chem. Soc. Dalton Trans. (1995) 497.
[118] J. Vicente, M.T. Chicote, M.D. Abrisqueta, unpublished results.
[119] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna, E. Olmos, J. Chem. Soc. Dalton Trans. (1994) 2891.