

NEW WAYS FOR THE PREPARATION OF HETEROCYCLIC GOLD(III) COMPLEXES

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Summary

The reaction of 1,2-dimethyl-2,3,4,5-tetraphenylstannacyclopentadiene $[(\text{Ph}_4\text{C}_4)\text{SnMe}_2]$ with $\text{AuCl}_3(\text{tht})$ (tht = tetrahydrothiophen) leads to the auracyclopentadiene complexes $[(\text{Ph}_4\text{C}_4)\text{AuCl}(\text{tht})]$ or $[(\text{Ph}_4\text{C}_4)\text{AuCl}]_2$, which react with $\text{Ti}(\text{acac})$ to give the complex $[(\text{Ph}_4\text{C}_4)\text{Au}(\text{acac})]$. Reaction of the latter with protonated ligands (HXL) or ($\text{H}_2\text{X}_2\text{L}_2$) leads to the formation of neutral mononuclear or binuclear complexes of the types $[(\text{Ph}_4\text{C}_4)\text{Au}(\text{XL})]$ (where XL is a monoanionic bidentate ligand) or $[(\text{Ph}_4\text{C}_4)\text{Au}(\text{X}_2\text{L}_2)\text{Au}(\text{Ph}_4\text{C}_4)]$ (where X_2L_2 is a dianionic tetradentate ligand). Reaction of the acetylacetonate complex with ammonium or pyridinium salts (LH^+X^-) gives the mononuclear neutral complexes $[(\text{Ph}_4\text{C}_4)\text{Au}(\text{X})(\text{L})]$ ($\text{X} = \text{CH}_3\text{COO}$ or CF_3COO ; $\text{L} = \text{NH}_3$ or py) or the cationic complexes $[(\text{Ph}_4\text{C}_4)\text{AuLL}']\text{X}$ when X is an anion with poor coordinating capacity ($\text{X} = \text{ClO}_4$ or BF_4) and the reaction is carried out in the presence of a neutral ligand ($\text{L}' = \text{PPh}_3$).

Introduction

Organotin compounds have found extensive use as intermediates in the preparation of organometallic compounds [1], but to the best of our knowledge they have only once been employed in the synthesis of organogold complexes; this was when we used a dibenzostannole compound for preparing heterocarbocyclic gold(III) and platinum(II) complexes [2].

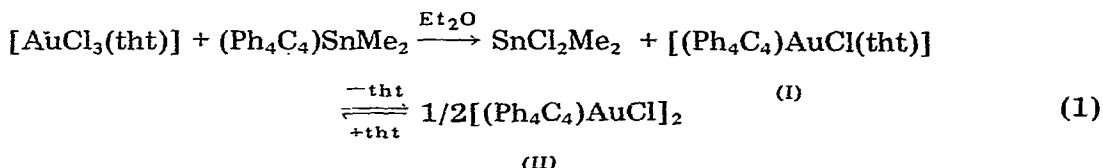
Several authors [3] have studied the synthesis of tetraphenylmetalla-cyclopentadiene complexes. Most of such compounds can be obtained by one of two routes; a) by the reaction of 1,4-dilithium-1,2,3,4-tetraphenylbutadiene with a dihalogeno compound, or b) by the reaction of diphenylacetylene with a complex of a transition metal in a low oxidation state.

In the present paper we describe a method for the preparation of 2,3,4,5-tetraphenylauracyclopentadiene complexes and their derivatives, based on the

use of 1,1-dialkyl-2,3,4,5-tetraphenylstanna-cyclopentadiene which has previously been used for the synthesis of pentaphenylborole [3], and which seemed of interest because of so few heterocyclic gold compounds were known [4]. Some of these results has been the subject of a preliminary communication [5].

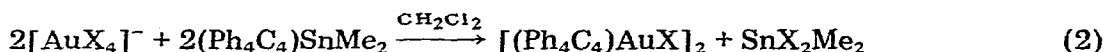
Results and discussion

The reaction between $[\text{AuCl}_3(\text{tht})]$ and $(\text{Ph}_4\text{C}_4)\text{SnMe}_2$ in ether (eq. 1) leads to the formation of a brick-red precipitate, which was identified as a mixture of $[(\text{Ph}_4\text{C}_4)\text{AuCl}(\text{tht})]$ (I) and $[(\text{Ph}_4\text{C}_4)\text{AuCl}]_2$ (II). The proportion of I to II varies with the conditions, but the combined yield reaches a maximum (~95%) after 20 minutes.



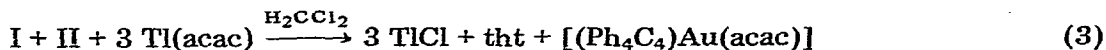
The separation of these complexes can be achieved by making use of the solubility of I in dichloromethane, in which the equilibrium is only slowly established. Moreover, addition of tht to the mixture of I and II, or to complex II alone, in dichloromethane gives complex I, while an ether suspension of I transformed in a few hours into an equilibrium mixture of I and II.

While treatment of 1,4-dilithium-1,2,3,4-tetraphenylbutadiene with $\text{AuCl}_3(\text{tht})$ leads to metallic gold and with $(\text{Bu}_4\text{N})[\text{AuCl}_4]$ gives metallic gold along with $(\text{Bu}_4\text{N})[\text{AuCl}_2]$ and unreacted $(\text{Bu}_4\text{N})[\text{AuCl}_4]$, the reaction between the stannole derivative $(\text{Ph}_4\text{C}_4)\text{SnMe}_2$ and $(\text{Bu}_4\text{N})[\text{AuCl}_4]$ or $(\text{Bu}_4\text{N})[\text{AuBr}_4]$ in dichloromethane proceeds according to eq. 2 to give complex II or



$[(\text{Ph}_4\text{C}_4)\text{AuBr}]_2$ (III), respectively, although the latter is obtained in lower yields. Complexes II and III are only very slightly soluble in organic solvents, which precludes the determination of their molecular weights. Nevertheless, it seems reasonable to assume a dimeric structure, as proposed for organometallic compounds of the type AuR_2X (R = alkyl; X = halogen) [4]. Moreover, II reacts with NaOH in acetone to give $[(\text{Ph}_4\text{C}_4)\text{Au}(\text{OH})]_2$, a dimeric complex with two OH bridging groups [6].

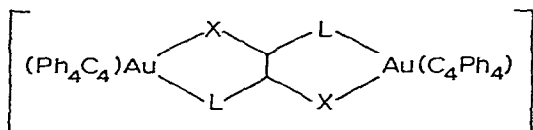
Complexes I and II show similar behaviour towards neutral ligands: Thus, displacement of the tht group of I and cleavage of the bridges of II take place readily. Since it is immaterial whether these reactions are carried out with I, with II, or with mixtures of both, and since process 1 always gives high yields, both complexes can be considered excellent precursors for the preparation of a large number of auracyclo-pentadiene complexes. Thus, the reaction of I or II with $\text{Ti}(\text{acac})_3$ in dichloromethane (eq. 2) gives a precipitate of TiCl , and $[(\text{Ph}_4\text{C}_4)\text{Au}(\text{acac})]$ (IV) can be isolated in 80% yield.



(The compound $[\text{AuMe}_2(\text{acac})]$ was the only gold(III) acetylacetonate complex previously reported [7]).

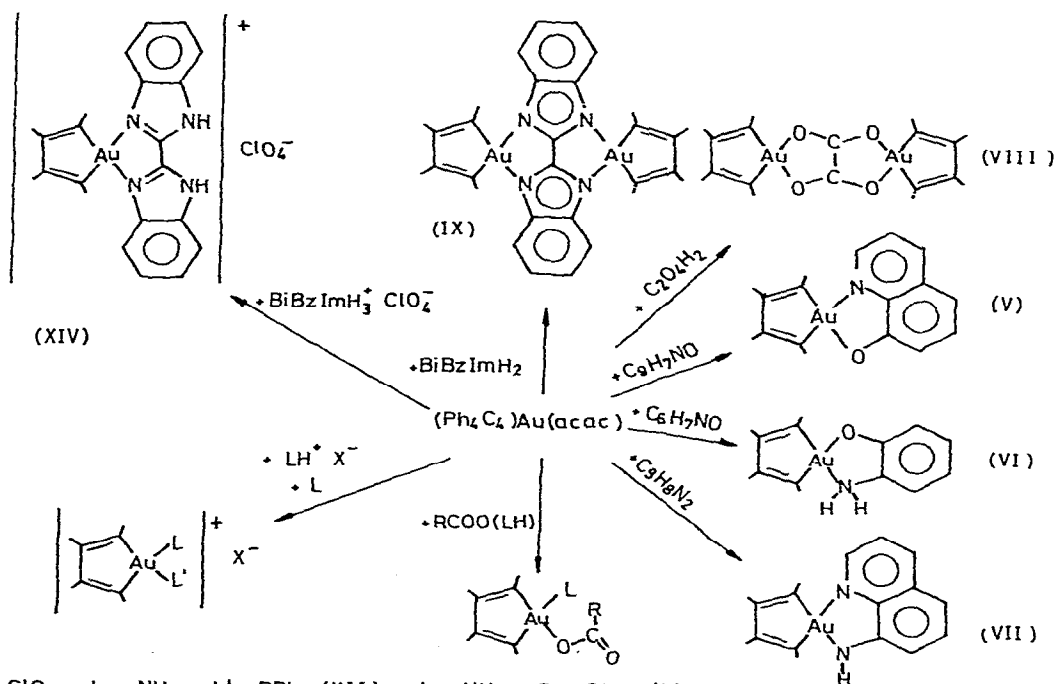
On treating IV with protonated ligands the acac^- group is readily replaced by a series of bidentate mononegative $(\text{X}-\text{L})^-$, or tetradentate dinegative ligands $(\text{X}_2\text{L}_2)^{2-}$. In this way, neutral mononuclear complexes of the type $(\text{Ph}_4\text{C}_4)\text{-}$

$\text{Au} \begin{array}{c} \text{X} \\ | \\ \text{L} \end{array} [\text{HX}-\text{L} = 8\text{-hydroxyquinoline, C}_9\text{H}_6\text{NOH (V); 2-aminophenol C}_6\text{H}_6\text{NOH (VI); 8-aminoquinoline, C}_9\text{H}_7\text{N}_2\text{H (VII)}] \text{ or neutral binuclear complexes of the type}$



$[\text{H}_2\text{X}_2\text{L}_2 = \text{oxalic acid, H}_2\text{C}_2\text{O}_4 \text{ (VIII); 2,2'-bibenzimidazole, C}_{14}\text{H}_8\text{N}_4\text{H}_2 \text{ (IX)}]$ are obtained in 70–100% yields. They can be isolated without difficulty because of the high solubility of the other product, $[\text{Hacac}]$, in organic solvents.

Treatment with reagents of the type HL^+X^- ($\text{HL}^+ = \text{ammonium or pyridinium; X}^- = \text{CH}_3\text{COO}^- \text{ or } \text{CF}_3\text{COO}^-$) leads to the neutral complexes $[(\text{Ph}_4\text{C}_4)\text{-}$



$\text{X} = \text{ClO}_4^-$, $\text{L} = \text{NH}_3$, $\text{L}' = \text{PPh}_3$ (XII)

$\text{L} = \text{NH}_3$, $\text{R} = \text{CH}_3$ (X)

$\text{X} = \text{BF}_4^-$, $\text{L} = \text{Py}$, $\text{L}' = \text{PPh}_3$ (XIII)

$\text{L} = \text{Py}$, $\text{R} = \text{CF}_3$ (XI)

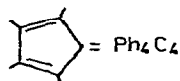


TABLE 1
ANALYTICAL AND SPECTRAL DATA

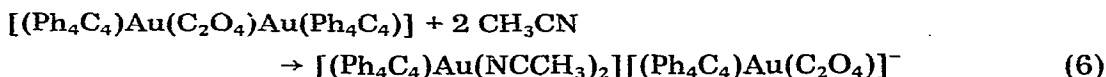
Complex	Elemental analysis Found (Calcd.) (%)				M.p. (°C)	Λ_M^a ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	M.w. ^b Found (calcd.)
	C	H	N	Au			
I [(Ph ₄ C ₄)AuCl(tht)]	56.48 (56.76)	4.42 (4.19)	—	20.18 (20.09)	143(d)	0.4	702 ^e (677)
II [(Ph ₄ C ₄)AuCl] ₂	56.52 (57.11)	3.39 (3.42)	—	33.67 (33.45)	188(d)	c	c
III [(Ph ₄ C ₄)AuBr] ₂	52.29 (53.10)	3.36 (3.18)	—	30.72 (31.10)	221(d)	c	c
IV [(Ph ₄ C ₄)Au(acac)]	59.72 (60.74)	4.02 (4.17)	—	30.20 (30.18)	189(d)	1.7	674 ^e (652)
V [(Ph ₄ C ₄)Au(C ₉ H ₆ NO)]	63.88 (63.71)	3.95 (3.76)	2.41 (2.01)	27.74 (28.23)	145(d)	4.0	625 ^e (697)
VI [(Ph ₄ C ₄)Au(C ₆ H ₆ NO)]	61.33 (61.73)	4.07 (3.96)	2.20 (2.12)	29.14 (29.77)	161(d)	0	702 (662)
VII [(Ph ₄ C ₄)Au(C ₉ H ₇ N ₂)]	64.01 (63.80)	3.97 (3.91)	4.22 (4.02)	28.19 (28.27)	219(d)	0.2	742 (697)
VIII [(Ph ₄ C ₄)Au(C ₂ O ₄)Au(Ph ₄ C ₄)]	57.76 (58.30)	3.41 (3.37)	—	33.27 (32.97)	183(d)	21.9 ^d	1361 (1195)
IX [(Ph ₄ C ₄)Au(BiBzIm)Au(Ph ₄ C ₄)]	62.42 (62.78)	3.83 (3.61)	4.14 (4.18)	30.13 (29.42)	196	1.4	1435 ^e (1340)
X [(Ph ₄ C ₄)Au(OOCCCH ₃ (NH ₃)]	57.50 (57.24)	4.52 (4.16)	2.52 (2.22)	30.94 (31.29)	202(d)	0.9	720 ^f (629)
XI [(Ph ₄ C ₄)Au(OOCCF ₃)(py)]	56.23 (56.38)	3.64 (3.38)	2.16 (1.88)	27.03 (26.42)	108(d)	2.6	742 (745)
XII [(Ph ₄ C ₄)Au(NH ₃)(PPh ₃)]ClO ₄	59.15 (59.27)	4.03 (4.11)	1.48 (1.50)	21.54 (21.13)	139	138.8	
XIII [(Ph ₄ C ₄)Au(py)(PPh ₃)]BF ₄	62.48 (62.40)	4.24 (4.11)	1.25 (1.43)	19.80 (20.06)	122(d)	134.7	
XIV [(Ph ₄ C ₄)Au(BiBzImH ₂)]ClO ₄	57.63 (56.86)	3.56 (3.41)	6.21 (6.31)	21.84 (22.20)	175(d)	124.0	

^a In acetone unless otherwise stated. ^b In chloroform unless otherwise stated. ^c Not soluble enough for determination. ^d In acetonitrile. ^e In benzene. ^f See text.

$\text{Au}(\text{CH}_3\text{COO})(\text{NH}_3)]$ (X) or $[(\text{Ph}_4\text{C}_4)\text{Au}(\text{CF}_3\text{COO})(\text{C}_5\text{H}_5\text{N})]$ (XI) along with Hacac. The cationic complexes $[(\text{Ph}_4\text{C}_4)\text{Au}(\text{NH}_3)(\text{PPh}_3)]\text{ClO}_4$ (XII) or $[(\text{Ph}_4\text{C}_4)\text{Au}(\text{py})(\text{PPh}_3)]\text{BF}_4$ (XIII) are obtained if the reactions are carried out in the presence of a neutral ligand, such as PPh_3 and if the anion of the salt is a poorly coordinating ligand ($\text{X}^- = \text{ClO}_4^-$ or BF_4^-). If the cation of the salt is bidentate, as e.g. in bibenzimidazolium perchlorate, no additional ligand is necessary, and the cationic complex $[(\text{Ph}_4\text{C}_4)\text{Au}(\text{BiBzImH}_2)]\text{ClO}_4$ (XIV) is formed directly.

All the reactions are summarized in Scheme 1. The reaction of the acetylacetonate complex with protonated ligands has previously been used in the synthesis of complexes [8] but never for those of gold. The only previously known gold(III) complexes with these O- and/or N-ligands are $[\text{AuMe}_2(\text{C}_9\text{H}_6\text{NO})]$ [9], $[\text{Au}(\text{C}_9\text{H}_6\text{NO})_2]^+$ [10] and $[\text{Et}_2\text{Au}(\text{C}_2\text{O}_4)\text{AuEt}_2]$ [11], while the only previously known transition metal complexes with the ligand BiBzIm (as in IX) were one titanium and one copper derivative [12].

The analytical results (C, H, N and Au), conductivities and molecular weights of the novel complexes are in good agreement with the proposed formulae (see Table 1), although the conductivity of the oxalate complex VIII in acetonitrile ($\Lambda_M = 21.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) is much lower than expected for a 1 : 1 electrolyte ($120\text{--}160 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) [13]. It therefore seems likely that in solution the neutral species is in equilibrium with ionic species, as formulated in eq. 6.



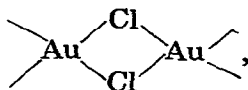
Furthermore, $[(\text{Ph}_4\text{C}_4)\text{Au}(\text{OOCCH}_3)(\text{NH}_3)]$ (X) gives a relatively high molecular weight in chloroform (found: 764, calculated 629), which points to an intermolecular association via a hydrogen bridge.

All the new complexes are thermally stable in the solid state and in solution, as also stable towards atmospheric moisture and daylight.

Infrared spectra

All the complexes show a series of absorptions characteristic of the $\text{Ph}_4\text{C}_4\text{Au}$ group [5] at 3060–3040 (two or three medium bands), 1600ms, 1310–1300w, 1180mw, 1160–1150w, 1030–1020m, 1000–990w, 920–910w, 790–780ms, 705–690 (two bands or a single broad one, vs), 640–630ms and 565–555ms cm^{-1} .

The chlorocomplex exhibits a strong band at 305 cm^{-1} , which by comparison with the bands observed for complexes with py (308 cm^{-1}) or PPh_3 (300 cm^{-1}), can be assigned to $\nu(\text{AuCl})$. Complex II shows two bands at 278m and 255 cm^{-1} ; which, in accord with the D_{2h} symmetry of the moiety



are assignable to $\nu(\text{AuCl})_{\text{bridge}}$. These values are consistent with the fact that bridging MX stretching frequencies are generally lower than terminal ones. Thus, the vibration due to $\nu(\text{AuCl})$ for *cis*- $[\text{AuMe}_2\text{ClL}]$ appears at 287–273

cm^{-1} [14], whilst the two bands due to $\nu(\text{AuCl})$ of complex $[\text{AuMe}_2\text{Cl}]_2$ appear at 273 and 245 cm^{-1} [15]. Analogously, the $\nu(\text{AuCl})$ of *cis*- $\text{Au}(\text{C}_6\text{F}_5)_2\text{-Cl}$ is observed at $\sim 320\text{ cm}^{-1}$ [16] while the corresponding bands of $[\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}]_2$ are at 300 and 285 cm^{-1} . These data stay that the *trans* influence follows the order $\text{Me} > \text{Ph}_4\text{C}_4 > \text{C}_6\text{F}_5$.

The IR spectrum of the bromo-complex III shows the beginning of an absorption near 200 cm^{-1} but the maximum cannot be seen. We assume that the bands assignable to $\nu(\text{AuBr})$ fall below the range of our instrument as observed for other gold(III) bromo-complexes [18].

The acetylacetonate complex IV exhibits three very strong bands at 1580, 1555 and 1520 cm^{-1} , which coincide with those observed for $[\text{AuMe}_2(\text{acac})]$ [19]. These bands are no longer present in the spectra of complexes V–XIV, which, however, show the absorptions due to the entering ligand. Thus, complex VI exhibits two sharp bands at 3338m and 3215 cm^{-1} , assignable to $\nu_{\text{asym}}(\text{NH})$ and $\nu_{\text{sym}}(\text{NH})$, while for complex VII the sharp band at 3405 cm^{-1} can be assigned to $\nu(\text{NH})$. The amino complexes X and XII show two bands assignable to $\nu_{\text{asym}}(\text{NH})$ and $\nu_{\text{sym}}(\text{NH})$ at 3160m and 3076m or 3320 m and 3245 cm^{-1} , respectively. The appreciable difference between the $\nu(\text{NH})$ frequencies of the complexes is likely to be due to the previously postulated presence of hydrogen-bridges in complex X, which would give rise to a shift of $\nu(\text{NH})$ towards lower energies [20]. Complex XIV shows several bands in the $3300\text{--}3000\text{ cm}^{-1}$ region, which must be associated well $\nu(\text{NH})$ and $\nu(\text{CH})$ of the 2,2'-bibenzoimidazole ligand. Most of these vibrations are not observed in the spectrum of the binuclear complex IX. Among the various possible bonding schemes of the 2,2'-bibenzoimidazole ligand in complex XIV, it seems reasonable to postulate coordination via the two nitrogen $=\text{N}-$, as observed for $[\text{Ni}(\text{BiImH}_2)(\text{H}_2\text{O})_2](\text{NO}_3)_2$ ($\text{BiImH}_2 = 2,2'\text{-biimidazole}$) [21].

In accord with the symmetry of the oxalate anion (D_{2h}) only two IR active bands due to $\nu(\text{CO})$ are to be expected for complex VIII, and they are observed at 1630vs(br) and 1350 m cm^{-1} . Comparable values have been observed for other similarly bridged oxalate complexes [22].

The acetato and trifluoroacetato complexes X and XI show bands at 1671s and 1355s or 1685s(br) and 1415 m cm^{-1} , respectively, which are assignable to $\nu_{\text{asym}}(\text{CO}_2)$ and $\nu_{\text{sym}}(\text{CO}_2)$. The difference between the two vibrations $\Delta\nu = \nu_{\text{asym}}(\text{CO}_2) - \nu_{\text{sym}}(\text{CO}_2)$ [$\Delta\nu = 336$ or 270 cm^{-1} , respectively] indicates monocoordination of these anions.

Experimental

IR spectra were recorded over the range $4000\text{--}200\text{ cm}^{-1}$ on a Perkin-Elmer 577 spectrophotometer using Nujol between polyethylene sheets or hexachlorobutadiene between NaCl windows. Conductivities were measured in $5 \times 10^{-4}\text{ M}$ solutions with a Philips PW9501/01 conductimeter. Molecular weights were determined with a Hitachi Perkin-Elmer Model 115 osmometer. Melting points were measured on a Buchi apparatus and are uncorrected. C, H and N analyses were carried out with a Perkin-Elmer 240 microanalyzer. Au was determined by ashing the samples together with an aqueous solution of hydrazine.

The starting materials $(\text{Ph}_4\text{C}_4)\text{SnMe}_2$ [23], $[\text{AuCl}_3(\text{tht})]$ [24], $\text{Bu}_4\text{N}[\text{AuX}_4]$ ($\text{X} = \text{Cl}$ or Br) [25] and BiBzImH_2 [26] were prepared by literature methods. $\text{Tl}(\text{acac})$ was obtained by refluxing a suspension of Tl_2CO_3 (4.0 g) and acetylacetone (5 ml) in ethanol (100 ml) for 12 h. The solution was filtered hot, then concentrated to 40 ml and cooled, to give crystalline $\text{Tl}(\text{acac})$, which was washed with 2×15 ml of ether (91% yield). The pyridine salts were prepared by adding stoichiometric amounts of the acid to ether solutions of pyridine. $[\text{BiBzImH}_2]\text{ClO}_4$ was obtained by the slow addition of an aqueous solution of perchloric acid to an acetone suspension of 2,2'-bibenzimidazole until most of the ligand had dissolved. The solution was filtered and evaporated to dryness, and the residue was washed with 2×10 ml of ether.

The other reagents were obtained from commercial sources.

All the solvents were distilled before use. The reactions were carried out at room temperature under magnetic stirring without any special precautions against daylight and moisture.

Reaction of $(\text{Ph}_4\text{C}_4)\text{SnMe}_2$ with $[\text{AuCl}_3(\text{tht})]$

To a suspension of $[\text{AuCl}_3(\text{tht})]$ (456 mg, 1.39 mmol) in 15 ml of ether was added $(\text{Ph}_4\text{C}_4)\text{SnMe}_2$ (705 mg, 1.39 mmol), and the mixture was stirred for 20 min. The precipitate was filtered off and washed with 3×4 ml of dichloromethane and then 2×5 ml of diethyl ether, and the brick-red complex II was finally suction-dried (400 mg, 49% yield).

The yellow dichloromethane and ether filtrate were concentrated to 10 ml, 20 ml of n-hexane were added, and the solution was again concentrated to 25 ml to give a yellow precipitate, which was washed with 2×3 ml of ether and suction-dried (440 mg, 46% yield).

Complex I can also be synthesized by treating complex II with tht in dichloromethane and following the above procedure.

$[(\text{Ph}_4\text{C}_4)\text{AuBr}]_2$ (III)

To a solution of $\text{Bu}_4\text{N}[\text{AuBr}_4]$ (137 mg, 0.18 ml) in 20 ml of acetone was added $(\text{Ph}_4\text{C}_4)\text{SnMe}_2$ (110 mg, 0.22 mmol). After 16 h stirring the solution (which is assumed to contain $[(\text{Ph}_4\text{C}_4)\text{AuBr}_2]^-$) was concentrated to 2 ml. Addition of 15 ml of ether gave an orange precipitate of complex III, which was filtered off, washed successively with 10 ml of water and 2×30 ml of methanol, and suction-dried (80 mg, 35% yield).

Similar work-up and starting from $\text{Bu}_4\text{N}[\text{AuCl}_4]$ gave complex II, but only in low yield (25%).

$[(\text{Ph}_4\text{C}_4)\text{Au}(\text{acac})]$ (IV)

A suspension of complex I in 20 ml of dichloromethane, or a solution of complex II in the same solvent was treated with a stoichiometric amount of $\text{Tl}(\text{acac})$. After 30 min stirring the precipitated TlCl was filtered off. The filtrate was concentrated to 5 ml, and 20 ml of hexane were added. The yellow precipitate (complex IV) was recrystallized from dichloromethane/hexane (80% yield).

Reaction of $(Ph_4C_4)Au(acac)$ with protonated ligands

Preparation of complexes V-VII. To suspensions of complex IV (~ 0.1 mmol) in 20 ml of ether were added stoichiometric amounts of the protonated ligands. After 1–2 h stirring the required complexes either precipitated spontaneously (the yellow complex V and the red complex VII) or precipitated after concentration to 2 ml and addition of 20 ml of n-hexane (the yellow complex VI). The three compounds were recrystallized from dichloromethane/n-hexane. (yields: 100% (V), 80% (VI), or 85% (VII)).

Preparation of complexes VIII and IX. To suspensions of complex IV (~0.1 mmol) in 20 ml of dichloromethane were added stoichiometric amounts of protonated ligands. After 16 h stirring the solutions were concentrated to 2 ml and 20 ml of ether or n-hexane were added to precipitate the yellow complexes VII or IX. The former was recrystallized from dichloromethane/acetone and the latter from dichloromethane/hexane (Yields: 72% (VIII) and 77% (IX)).

Preparation of complexes X–XIV. To suspensions of complex IV (~0.1 mmol) in 20 ml of acetone were added stoichiometric amounts of the protonated ligands. (For the preparation of complexes XII and XIII a stoichiometric amount of PPh_3 had previously been added). After 1–2 h stirring the solutions were concentrated to 2 ml and n-hexane was added to precipitate the yellow complexes. (Yields: 88% (X), 73% (XI), 58% (XII), 74% (XIII) and 72% (XIV)).

Complexes XII and XIV show bands around 1100vs(br) and 620m cm^{-1} , whilst XIII exhibits bands at 1050vs(br) and 560s cm^{-1} . These frequencies indicate that there is no coordination of the ClO_4^- and BF_4^- anions.

References

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