

A Facile, Novel Way to Prepare Anionic, Neutral and Cationic Gold(I) Complexes†

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The complex $\text{ppn}[\text{Au}(\text{acac})_2]$ **1** can be obtained by reacting $\text{ppn}[\text{AuCl}_2]$ with $[\text{Ti}(\text{acac})]$ in 1 : 2 molar ratio,† and complex **1** reacts with compounds of the type RH in which H has some acidic character to give the corresponding $[\text{AuR}_2]^-$ species; RH = $\text{CH}_2(\text{CN})_2$, $\text{CH}_2(\text{CO}_2\text{Me})_2$ **3**, $\text{CH}_2(\text{CN})\text{CO}_2\text{Me}$ **4**, Me_3SiCCH **5**, 2-SH- $\text{C}_5\text{H}_4\text{N}$ **6**, AuR RH = $\text{CH}_2(\text{PPh}_2)_2$, **7**, or $[\text{AuR}_2]^+ \text{RH} = [(\text{4-MeC}_6\text{H}_4)_3\text{PCH}_2\text{C}_5\text{H}_4\text{N-2}]\text{ClO}_4$ **8**.

Anionic dialkylaurate(I) complexes are very scarce in the literature¹ and, among them, only the homoleptic $[\text{AuMe}_2]^-$ seems to have been isolated as the $[\text{Li}(\text{py})_2]^+$ or $[\text{Li}(\text{pmdt})]^+$ salt.^{2,3} The synthesis of both requires the use of LiMe and, once isolated, they are rather unstable.

According to Schmidbauer,¹ these type of complexes deserve considerable theoretical interest since they represent one of the simplest organometallic groups. The coordination number two and the linear arrangement provide ideal conditions for theoretical treatment of both bonding and reaction mechanisms.⁴

Here we report the preparation of $\text{ppn}[\text{Au}(\text{acac})_2]$ **1**, the first homoleptic air-stable dialkylaurate(I), and its use as a versatile precursor for anionic, neutral and cationic complexes, and among them dialkylaurate(I) derivatives.

We have previously shown that the basic acac ligand present in $[\text{Au}(\text{acac})(\text{PPh}_3)]$ is able to deprotonate phosphonium salts yielding $[\text{Au}\{\text{CH}(\text{PPh}_3)\text{C}(\text{O})\text{R}\}(\text{PPh}_3)]^+$ and $[(\text{AuPPh}_3)_2\{\mu\text{-C}(\text{PPh}_3)\text{C}(\text{O})\text{R}\}]^+$ complexes (R = Me, Ph, OMe, OEt, NMe₂).⁵ Thus, the use of $[\text{Au}(\text{acac})(\text{PPh}_3)]$ allowed the synthesis of complexes with very poor donor ligands (*i.e.* carbonyl-stabilized ylides) taking advantage of the fact that their conjugate acids are strong enough to react with the acac-complex. Since then we have attempted to prepare a $[\text{Au}(\text{acac})_2]^-$ complex which would permit the synthesis of homoleptic complexes by deprotonation of compounds containing somewhat acidic hydrogen atoms.

The complex $\text{ppn}[\text{Au}(\text{acac})_2]$ **1** can be obtained by reacting $\text{ppn}[\text{AuCl}_2]$ with $[\text{Ti}(\text{acac})]$ in 1 : 2 molar ratio.‡ This compound is surprisingly stable in the solid state, although it slowly decomposes in solution. **1** reacts with an excess of malononitrile, dimethyl malonate, or methyl cyanoacetate to give the corresponding dialkylaurate(I) derivatives $\text{ppn}[\text{Au}\{\text{CH}(\text{R})\text{R}'\}_2]$ (**2**, R = R' = CN; **3**, R = R' = CO₂Me; **4**, R = CN, R' = CO₂Me§). Compound **2** is extraordinarily stable while **3** and **4**, which are stable at 0°C, decompose slowly at room temperature.

In order to define the scope of this synthetic method, we have tried reactions of **1** with other types of ligands, namely, trimethylsilylacetylene, 2-mercaptopyridine, 1,2-bis(diphenylphosphino)methane and 2-pyridylmethyltri-*p*-tolylphosphonium perchlorate.

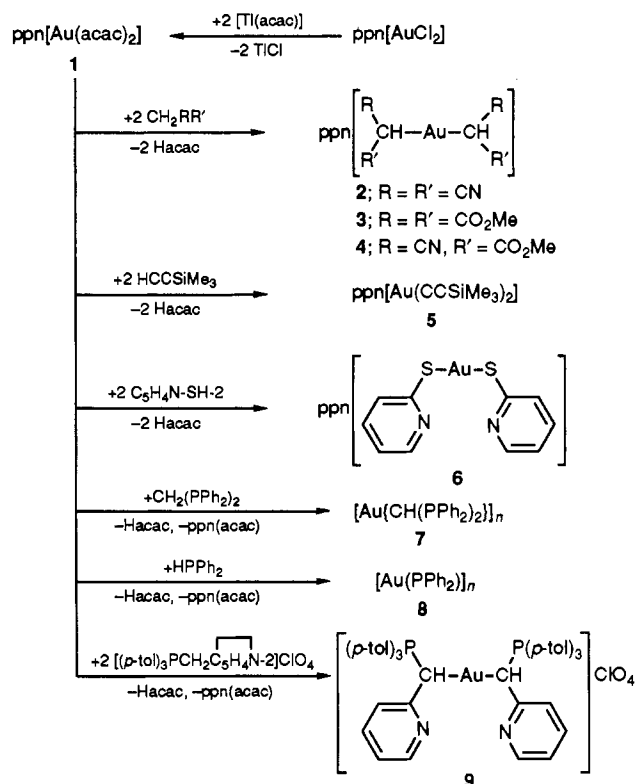
Reaction of **1** with Me_3SiCCH gives $\text{ppn}[\text{Au}(\text{CCSiMe}_3)_2]$ **5**§ one of the few alkynylgold(I) derivatives described.⁶ Among them, only $[\text{Au}(\text{CCPh})_2]$ (Q = PPh₄, ppn) are of the same type as **5**, and their reported syntheses require the use of liquid

NH_3 , which contrasts with the simplicity of our method. On the other hand, the presence of the SiMe₃ moiety in complex **5** offers a new interesting reactivity centre.

The reaction of **1** with the classical coordination ligand 2-mercaptopyridine affords $\text{ppn}[\text{Au}(\text{C}_5\text{H}_4\text{NS})_2]$ **6**§. The preference of gold(I) with respect to N-donor ligands is well known and this coordination mode is observed in other related mercaptopyridine gold(I) complexes.⁷ Similar reactions take place with other mercapto-derivatives, and the resulting products are being characterized. Gold complexes such as those have been used in the treatment of arthritis.⁸

Compound **1** reacts with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ or with HPPH₂ to give the previously described polymeric complexes $[\text{Au}\{\text{CH}(\text{PPh}_2)_2\}]_n$ **7**¶ synthesized using the Li-derivative⁹ again or $[\text{Au}(\text{PPh}_2)]_n$ **8**.¶,10

Finally, the cationic complex $[\text{Au}\{\text{CH}[\text{P}(\text{4-MeC}_6\text{H}_4)_3]\text{-C}_5\text{H}_4\text{N-2}\}_2]\text{ClO}_4$ **9**§ can be obtained by reacting **1** with $[(\text{4-MeC}_6\text{H}_4)_3\text{PCH}_2\text{C}_5\text{H}_4\text{N-2}]\text{ClO}_4$ in a 1 : 2 molar ratio. We



Scheme 1

† Abbreviations used: ppn = bis(triphenylphosphoranylidene) ammonium; Hacac = pentane-2,4-dione; py = pyridine; pmdt = *N,N,N',N',N''*-pentamethyldiethylenetriamine; *p*-tol = *p*-MeC₆H₄.

‡ The white complex **1** was obtained by the reaction of $\text{ppn}[\text{AuCl}_2]$ with $[\text{Ti}(\text{acac})]$ (1 : 2) in CH_2Cl_2 at room temperature (85% yield). Satisfactory elemental analyses were obtained, m.p. 90°C decomp.; $\Lambda_M = 97 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ($3 \times 10^{-4} \text{ mol dm}^{-3}$ in acetone); $\nu(\text{CO})/\text{cm}^{-1}$, 1640vs; ¹H NMR (CDCl₃, SiMe₄ as reference, 300 MHz): δ 2.34 (s, 6H, Me), 4.35 (s, 1H, CH), 7.41–7.71 (m, 15H, Ph).

§ These complexes have been characterized by their IR spectrum, ¹H, ³¹P{¹H}, ¹³C{¹H} NMR spectra, and elemental analyses. All the data confirm the proposed structures.

¶ Data for complexes **7** and **8** agree with those reported for $[\text{Au}\{\text{CH}(\text{PPh}_2)_2\}]_n$ and $[\text{Au}(\text{PPh}_2)]_n$ respectively. See ref. 9 and 10.

foresee that many other RH compounds will react with $\text{ppn}^+ + [\text{Au}(\text{acac})_2]$ to give other cationic complexes.

The reactivity of **1** towards other hydrogenated species is currently being examined.

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