

Tris(pentafluorophenyl)(tetrahydrothiophen)gold(III)

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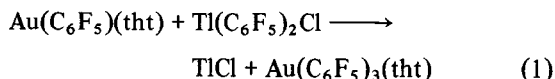
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Although trialkyl-gold complexes are reasonably represented in the chemistry of this metal [1], the only hitherto known triaryl-gold derivatives are $\text{Au}(\text{C}_6\text{F}_5)_3\text{PPh}_3$ [2], $\text{Au}(\text{C}_6\text{F}_5)_2(\text{C}_6\text{Br}_5)\text{PPh}_3$ [3] and $\text{Bu}_4\text{N}[\text{Au}(\text{C}_6\text{F}_5)_3\text{Br}]$ [4].

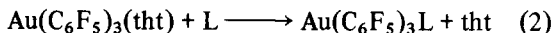
In the present paper we describe the preparation of $\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})$ and the results obtained on studying the displacement of its tetrahydrothiophen group (tht) by other mono- or bidentate, neutral or anionic ligands, which has led to the synthesis of novel tris(pentafluorophenyl)gold(III) derivatives.

Refluxing of a benzene solution of $\text{Au}(\text{C}_6\text{F}_5)(\text{tht})$ [4] with an equimolecular amount of $\text{Ti}(\text{C}_6\text{F}_5)_2\text{Cl}$ leads to the oxidation of the gold(I) compound and precipitation of TiCl_4 , as may be seen from eqn. (1)



The resulting gold(III) complex, which is isolated (82% yield) as a white air- and moisture-stable solid, is an excellent precursor for the preparation of new tris(pentafluorophenyl)gold(III) complexes since, as we have recently shown for $\text{Au}(\text{C}_6\text{F}_5)(\text{tht})$ [4, 6] the tht group can readily be displaced by other ligands.

Thus, the reaction with equimolecular amounts of mono- or bidentate neutral ligands, such as PPh_3 , AsPh_3 , 1,2-bis(dimethylarsino)benzene, (diars), or bis(diphenylphosphino)methane, (dpm), leads, according to eqn. (2), to complexes of the type $\text{Au}(\text{C}_6\text{F}_5)_3\text{L}$

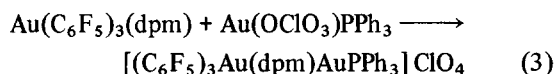


which can be isolated (70–80% yield) as white solids, and are non-conducting in acetone and monomeric in benzene.

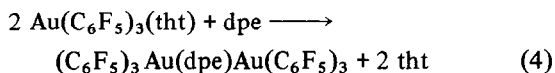
For $\text{L} = \text{diars}$, if the reaction is continued for more than five minutes, a progressive reduction can be observed which leads to $[\text{Au}(\text{diars})_2][\text{Au}(\text{C}_6\text{F}_5)_2]$ [7] (After 1 h stirring at room temperature the gold(I) complex is obtained in 24% yield). The ^1H NMR spectrum of $\text{Au}(\text{C}_6\text{F}_5)_3(\text{diars})$ (in CDCl_3 , 100 MHz) shows only two peaks at $\tau = 2.57$ (m, 4H, C_6H_4) and $\tau = 8.41$ (s, 12H, AsMe), whilst its ^{13}C NMR spectrum (CDCl_3 , ^1H decoupled, 21.15 MHz)

consisted of three peaks at δ 141.7 (C–As), 130.5 (*ortho*- and *meta*-C) and 11.7 (As–CH₃) p.p.m., indicating the complete equivalence of the two As–ends. On the other hand, these values are similar to those found for $[\text{Au}(\text{diars})_2][\text{Au}(\text{C}_6\text{F}_5)_2]$, whose diars groups act, as we have recently shown [7], as bidentate ligands and the Au atom in $(\text{C}_6\text{F}_5)_3\text{Au}(\text{diars})$ should therefore be pentacoordinated.

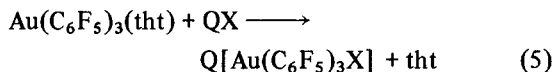
For $\text{L} = \text{dpm}$, however, we meet an entirely different situation: its ^{31}P NMR spectrum (CDCl_3 , 40.48 MHz) shows two resonances at -14.3 (d of m) and $+30.8$ (d, $J_{\text{P-P}} = 65$ Hz) p.p.m. (rel. ext. H_3PO_4), which indicates that only one of its two phosphorus atoms is coordinated to the gold atom, whilst the other is practically free. This suggests the possibility of coordinating another metal atom to the free end of the diphosphine. Attempts to prepare $(\text{C}_6\text{F}_5)_3\text{Au}(\text{dpm})\text{Au}(\text{C}_6\text{F}_5)_3$ proved unsuccessful and after two hours stirring at room temperature of a dichloromethane solution of equimolecular amounts of $\text{Au}(\text{C}_6\text{F}_5)_3(\text{dpm})$ and $\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})$ we recovered the unchanged starting products. Nonetheless, the reaction between $\text{Au}(\text{C}_6\text{F}_5)_3(\text{dpm})$ and $\text{Au}(\text{OCIO}_3)\text{PPh}_3$ leads to the displacement of the perchlorato group and formation of a binuclear complex whose gold(III) and gold(I) atoms are bridged by the diphosphine ligand, eqn.(3)



1,2-bis(diphenylphosphino)ethane, (dpe), shows again a different behaviour and its addition to a dichloromethane solution of $\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})$ (0.5:1 or higher molar ratio) leads to the binuclear complex $(\text{C}_6\text{F}_5)_3\text{Au}(\text{dpe})\text{Au}(\text{C}_6\text{F}_5)_3$ (see Table I)



The tht ligand can also readily be replaced by halo- or pseudohalo-ions, and thus the reaction with $[\text{Et}_4\text{N}]\text{Cl}$ or $[\text{BzPh}_3\text{P}]\text{SCN}$ leads, according to eqn. (5), to the formation of tris(pentafluorophenyl)-aurate(III) complexes:



They are white air- and moisture-stable solids, whose conductance in acetone is that of 1:1 electrolytes. For $\text{X} = \text{Cl}$ the vibration due to $\nu(\text{Au-Cl})$ is located at 325 cm^{-1} . For $\text{X} = \text{SCN}$ (Nujol suspension) the $\nu(\text{C}\equiv\text{N})$ absorption is observed at 2125 cm^{-1} and determination of the internal standard ratio [9] gives 0.3, which confirms an S-bonded structure of the complex. In dichloromethane solution, however, we observe along with the strong band at 2120 cm^{-1} , a weaker one at 2070 cm^{-1} . This has already been reported [10] for gold(I) thiocyanato complexes and

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TABLE I. Properties of the Novel Complexes.

Complex		M.p. (°C)	Λ_M^a	Mol.wt ^b Found (Calcd.)
I	Au(C ₆ F ₅) ₃ (tht)	190	11	658(786)
II	Au(C ₆ F ₅) ₃ AsPh ₃	98(d)	21	1039(1001)
III	Au(C ₆ F ₅) ₃ (diars)	157	12	1014(984)
IV	Au(C ₆ F ₅) ₃ (dpm)	185	2	1110(1082)
V	[(C ₆ F ₅) ₃ Au(dpm)AuPPh ₃]ClO ₄	186(d)	156	—
VI	(C ₆ F ₅) ₃ Au(dpe)Au(C ₆ F ₅) ₃	255(d)	1	1855(1794)
VII	Et ₄ N[Au(C ₆ F ₅) ₃ Cl]	192(d)	117	—
VIII	BzPh ₃ P[Au(C ₆ F ₅) ₃ SCN]	116(d)	102	—

^aIn acetone, ohm⁻¹ cm² mol⁻¹. ^bIn benzene.

should correspond to the presence of the Au—NCS isomer (ratio of the areas Au—NCS/Au—SCN= 0.64) in the solution.

In previous papers [11] we have shown that the absorption at *ca* 800 cm⁻¹ in pentafluorophenyl complexes acts as if it was due to a C—M stretching vibration. This observation proves also to be true for the herein described tris(pentafluorophenyl) derivatives, which are characterized by the presence of three bands located at approx 805 (m), 795 (m) and 780 (m) cm⁻¹, though the last two absorptions merge sometimes into a broad, asymmetric band.

References

- 1 R. J. Puddephatt 'The Chemistry of Gold' Elsevier Amsterdam (1978), p. 123.
- 2 L. G. Vaughan and W. A. Sheppard, *J. Organometal. Chem.*, **22**, 739 (1970).
- 3 R. Usón and A. Laguna, *Synth. React. Inor. Met-org. Chem.*, **5**, 17 (1975).
- 4 R. Usón, A. Laguna and J. Vicente, *J. Chem. Soc. Chem. Comm.*, 353 (1976); *J. Organometal. Chem.*, **131**, 471 (1977).
- 5 R. Usón, A. Laguna and T. Cuenca, *J. Organometal. Chem.*, in press.
- 6 R. Usón, A. Laguna, J. Vicente and J. Garcia, *Rev. Acad. Ciencias Zaragoza*, **31**, 77 (1976).
- 7 R. Usón, A. Laguna, J. Vicente, J. Garcia, P. Jones and G. M. Sheldrick, to be published.
- 8 E. E. Isaac and W. A. G. Graham, *Inorg. Chem.*, **14**, 2560 (1975); S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman and J. P. Jesson, *Inorg. Chem.*, **13**, 1095 (1974).
- 9 R. A. Bailey, T. W. Michelson and W. N. Mills, *J. Inorg. Nucl. Chem.*, **33**, 3206 (1971).
- 10 J. L. Burmeister and J. B. Melpolder, *J. Chem. Soc. Chem. Comm.*, 613 (1973).
- 11 R. Usón, J. Forniés, F. Martínez and M. Tomás, *J. Chem. Soc., Dalton*, (DAL, 9/996), in press; R. Usón, A. Laguna, J. Garcia and M. Laguna, *Inorg. Chim. Acta.*, **37**, 201 (1979).