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ORGANOGOLD CHEMISTRY
II*. TRIS(PENTAFLUOROPHENYL)GOLD(III)

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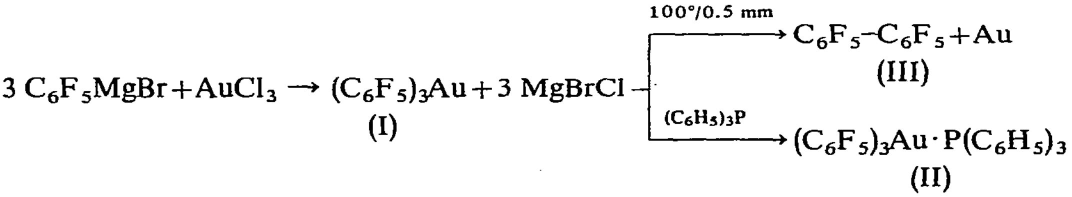
SUMMARY

Tris(pentafluorophenyl)gold(III) (I) has been prepared as a stable compound in ether solution at room temperature and has been characterized as the triphenylphosphine adduct (II). Attempted isolation of (I) gave metallic gold and decafluorobiphenyl.The ^{19}F NMR spectrum of (II) is analyzed in terms of structure and electronic properties and compared to similar measurements on the gold(I) derivatives.

RESULTS AND DISCUSSION

Stable organometallic compounds containing the pentafluorophenyl group have been reported for copper[2-5], cadmium[6], zinc[7], and gold[8,9]. We now report the preparation of tris(pentafluorophenyl)gold(III), (I), by addition of solid, anhydrous gold trichloride (9.9 mmoles) to 50 ml of an ether solution of pentafluorophenylmagnesium bromide (32.4 mmoles) at −60°. The gold trichloride gradually dissolved as the solution was allowed to warm to room temperature, and no metallic gold precipitated.



$$3\,C_6F_5MgBr + AuCl_3 \rightarrow \underset{(I)}{(C_6F_5)_3Au} + 3\,MgBrCl \begin{cases} \xrightarrow{100°/0.5\ mm} \underset{(III)}{C_6F_5\text{–}C_6F_5} + Au \\ \xrightarrow{(C_6H_5)_3P} \underset{(II)}{(C_6F_5)_3Au\cdot P(C_6H_5)_3} \end{cases}$$

The solution was stirred at room temperature for 18 h with no evidence of decomposition. After addition of 1 g of trimethylchlorosilane to react with excess Grignard reagent, triphenylphosphine (10.0 mmoles) was added to complex the product. A 55% yield of adduct (II) was obtained, m.p. 243–246° (decompn.), after recrystallization from cyclohexane. (Found: C, 45.47; H, 1.75; Au, 20.79; F, 29.77. $C_{36}H_{15}$Au-

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[*] For Part I see ref. 1.

$F_{15}P$ calcd.: C, 45.01; H, 1.58; Au, 20.51; F, 29.67%.) Compound (II) is stable to moisture and air.

The solution stability of (I) at room temperature contrasts sharply with that of trimethylgold(III)[10] [the only trialkyl- or triarylgold(III) compound previously reported] which decomposes in ether solution at −40 to −35° to ethane and methane. Tris(pentafluorophenyl)gold(III) undergoes a parallel decomposition at higher temperatures. Attempted sublimation of (I) from the residue remaining after solvent removal (no triphenylphosphine added) gave decafluorobiphenyl (III) (62% yield) and metallic gold. Since all known gold(III) compounds, both organic and inorganic, are four-coordinate[11] (or higher), (I) is undoubtedly complexed by ether in solution. Decomposition probably commences when the coordinating ether molecule is lost under the high vacuum conditions.

In related work, we have studied the reaction of aurous chloride with pentafluorophenylmagnesium bromide at 0° in ether. Metallic gold and decafluorobiphenyl are formed instantly, possibly via an unstable (pentafluorophenyl)gold(I) intermediate.

$$2\,C_6F_5MgBr + 2\,AuCl \rightarrow C_6F_5{-}C_6F_5 + 2\,MgBrCl + 2\,Au$$

We have recently reported (pentafluorophenyl)(triphenylphosphine)gold(I) as a stable compound[1].

The ^{19}F NMR chemical shifts* of tris(pentafluorophenyl)(triphenylphosphine)gold(III) (II) are reported in Table 1 with comparison to the chemical shifts for (pentafluorophenyl)(triphenylphosphine)gold(I) (IV). For compound (II), the patterns for the *o*- and *p*-fluorines each appear as two sets of peaks in relative intensity of two to one which we have assigned to the pentafluorophenyl groups in *cis* and *trans* positions, respectively**. The downfield shift for the *m*- and *p*-fluorines of (II) relative to (IV) are qualitatively as expected for +3 relative to +1 gold. The difference in *cis*

TABLE 1

^{19}F NMR CHEMICAL SHIFTS OF (PENTAFLUOROPHENYL)GOLD DERIVATIVES AND CALCULATED SUBSTITUENT PARAMETERS

Compound	Chemical shift[a]				
	Φ_o	Φ_m	Φ_p	σ_I	σ_R
$(C_6F_5)_3Au \cdot P(C_6H_5)_3$ *cis*	120.0	161.0	157.4	+0.63	−0.28
trans	122.0	161.0	156.4	+0.56	−0.24
$C_6F_5AuBr_2 \cdot P(C_6H_5)_3$	123.2	160.9	157.7	+0.68	−0.30
$C_6F_5Au \cdot P(C_6H_5)_3$	116.0	162.4	158.3	+0.29	−0.19
m-$FC_6H_4Au \cdot P(C_6H_5)_3$		2.32[b]		−0.25[c]	
p-$FC_6H_4Au \cdot P(C_6H_5)_3$			3.23[b,d]		−0.03[c]

[a] Chemical shifts of *o*-, *m*- and *p*-fluorines in ppm. The Φ scale[12] is based on C_6F_6 = 163.0 ppm upfield from $CFCl_3$. All measurements made at 5–10% concentration in benzene containing $CFCl_3$ reference. [b] ^{19}F shift in *m*- and *p*-fluorophenyl derivatives. [c] Calculated by methods of Taft and coworkers[16]. [d] This value is correct. The value of 3.32 in ref. 1 was a typographical error.

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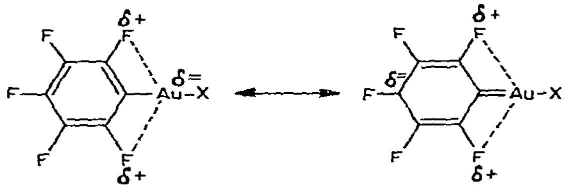
* For a recent analysis of ^{19}F spectra of pentafluorophenyl derivatives, including organometallic derivatives, see ref. 12.

** For a study of pentafluorophenyl derivatives of some transition metals, see ref. 13.

and *trans* shifts probably reflects a *trans* effect*. The upfield shift of the *o*-fluorines for (II) relative to (IV) is unexpected, but could be explained by a ring current shielding interaction of the adjacent pentafluorophenyl system. Because of non-bonded interactions with the *o*-fluorines, the pentafluorophenyl rings are probably oriented so that (II) looks like a propellar**. The *o*-fluorines on the *trans* ring are shifted further upfield because they are adjacent to two rings.

Following the literature method[12], the Φ_m and Φ_p values have been used to calculate the inductive and resonance parameters for the gold(I) and gold(III) substituents and these values are also given in Table 1. The values, particularly σ_I, calculated from the pentafluorophenyl chemical shift data do not agree with values calculated from ^{19}F shift data on *m*- and *p*-fluorophenyl(triphenylphosphine)gold(I)[1]. These results could be explained either by a paramagnetic effect or a through-space interaction between the *o*-fluorines and the gold. This *ortho* interaction would lead to considerable decrease in charge density on the *o*-fluorines (note the large downfield shift of the *o*-fluorines, much larger than observed for most other substituents other than transition metals). The net result of such an interaction would be increased negative charge in the gold which would enhance a $-R$ effect on the *p*-fluorine as observed. The through-space interaction of the positive *o*-fluorines would cause a downfield shift of the *m*-fluorines and an apparent increase of σ_I to a large positive value. This type of interaction between gold and the *o*-fluorines may be considered analogous to the addition of halogens such as bromine to gold(I) derivatives[1].



A paramagnetic effect also could explain the low field *o*-fluorine shifts, but considerable additional theoretical and experimental studies are needed to determine effects on the ^{19}F shifts in the other positions. In the gold(III) compounds the enhanced electron-withdrawing character shown by the large positive σ_I is expected from the $+3$ state of gold. The enhanced $-R$ effect by gold(III) is not easily explained.

These observations on the ^{19}F chemical shifts of the pentafluorophenylgold derivatives should be pertinent to interpreting interactions of fluorines from the pentafluorophenyl rings with other transition metals[12] and clearly points out deficiencies of using ^{19}F chemical shift measurements of the pentafluorophenyl ring for calculation of σ parameters.

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* The topic of the *trans* effect has been reviewed by Basolo and Pearson[14].

** An X-ray analysis[15] of chlorobis(pentafluorophenyl)(triphenylphosphine)gold(III) showed that the pentafluorophenyl rings are twisted 77° out of the coordination plane.

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