Fluorocarbon- and Carborane-Gold Complexes

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Summary The synthesis of fluorocarbon–gold complexes from Ph_3PAuMe is described, including the preparation of binuclear species $[Ph_3PAu]_2(AB)$ [$AB = (CF_3)_2CO$, $(CF_3)_2CNH$, and $(CF_3)_2C_2$]: whereas the gold–carbon bond in $Ph_3PAuC_2F_4Me$ is cleaved by bromine, a gold(III) complex $Ph_3PAu(C_2B_{10}H_{10}Ph)(Br)_2$ is obtained from $Ph_3PAu(C_2B_{10}H_{10}Ph)$, an example of a very stable new class of organogold(I) compound.

In studies on the use of d^{10}-complexes in the synthesis of organometallics, we have obtained several new organogold complexes which are themselves useful intermediates. U.v. irradiation of a mixture of methyl(triphenylphosphine)gold (I) and tetrafluoroethylene in benzene affords air stable, white crystalline $Ph_3PAuCF_2CF_2Me$ (II). In contrast, hexafluoroacetone reacts with (I) at room temperature to give a novel binuclear gold complex $Ph_3PAuC(CF_3)_2OAuPPh_3$ (III). The latter undergoes an unusual exchange reaction with hexafluoroisopropylidenimine giving $Ph_3PAuC(CF_3)_2$-$N(H)AuPPh_3$ (IV). Surprisingly, (IV) could not be obtained by treatment of (I) with $(CF_3)_2CNH$; only rapid reduction to metallic gold occurred. Hexafluorobut-2-yne also reacts with (I) to give a binuclear gold complex $[Ph_3PAu]_2C_2(CF_3)_2$ (V), there being no evidence for formation of the simple insertion product $Ph_3PAu[C_2(CF_3)_2]Me$. The ^{19}F n.m.r. spectrum of (V) consists of a multiplet centred at 54 p.p.m. (relative to CCl_3F) with a pattern typical of an $X_3AA'X'_3$ system, but poorly resolved, so that the coupling constants could not be evaluated. Nevertheless, either $J_{AA'}$ or $J_{XX'}$ is *ca.* 50 Hz, and the magnitude of this coupling establishes that it is the phosphorus nuclei which are strongly coupled and not the CF_3 groups.[1]

It has very recently been reported[2] that $Ph_3PAuC_6F_5$ (Au^I, d^{10}) reacts with bromine to give $Ph_3PAu(C_6F_5)(Br)_2$ (Au^{III}, d^8), together with some Ph_3PAuBr. Fluoroalkyl groups in gold(I) complexes such as (II) are readily cleaved by electrophilic reagents, so that organogold(III) complexes could not be obtained by this route. Bromine affords Ph_3PAuBr, and pentafluorobenzoic acid gives Ph_3PAuO_2-CC_6F_5. Above 120° the latter releases CO_2 and forms the compound $Ph_3PAuC_6F_5$.[2,3]

Our inability to obtain an organogold(III) dibromide by treating (II) with bromine contrasts also with the behaviour of a new class of organogold complex. A series of triphenylphosphinegold–carborane compounds $Ph_3PAuC_2B_{10}H_{10}R$ [R = H, Me, or Ph] have been prepared by treating Ph_3PAuCl with the lithio-derivative of the carborane. The gold derivatives are all white, crystalline solids, soluble in benzene, and have very high thermal stability. They may be heated at 130—200° before any decomposition occurs. The complex $Ph_3PAuC_2B_{10}H_{10}Me$ (VI) does not react with trifluoroacetic acid in benzene solution whereas (I) with this reagent affords $Ph_3PAuO_2CCF_3$ at room temperature. The unusual stability of gold–carborane σ-bonds is further illustrated by their failure to undergo insertion reactions with tetrafluoroethylene, and by the oxidative-addition reaction which occurs between 1-phenyl-2-(triphenylphosphinegold)-1,2-dicarbaclovododecaborane and bromine to give the gold(III) complex $Ph_3PAu(C_2B_{10}H_{10}Ph)(Br)_2$ (VII), [ν_{max} (Au–Br)[4] 209 and 264 cm^{-1}]. The stability of the gold–carborane bond may be related to the well-established electron-withdrawing[5] influence of the carborane group, so that addition of bromine is not followed by a reductive-elimination step.

(*Received, July 20th,* 1970; *Com.* 1165.)

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