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Preliminary communication

ARYLGOLD(I) AND ARYL(TRIPHENYLPHOSPHINE)GOLD(I) COMPOUNDS

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Summary

Novel monomeric benzyl- and aryl-gold(I) triphenylphosphine complexes have been prepared. Pure, uncomplexed 2-[(dimethylamino)methyl]-phenylgold(I) has been isolated from the reaction of tetranuclear bis $\{2-[(dimethylamino)methyl] phenyl\}$ goldlithium (R_4 Au₂ Li₂) with trimethyltin bromide.

Earlier we reported aryl-copper(I) [1] and -silver [2] compounds containing built-in ligands such as CH_2 NMe₂, NMe₂, OMe etc. The hydrocarbon-soluble compounds among these have discrete polynuclear structures in which aryl groups are bonded to a metal cluster by 2e-3c bonds [1b, 2a, 3] Recently we have isolated novel mixed gold(I)—metal compounds R_4 Au₂ Li₂ and R_4 Au₂ Cu₂ [4] which like the related compounds R_4 Cu₄ [3a], R_4 Cu₂ Li₂ [1b] and R_4 Ag₂ Li₂ [2a] (R=2-Me₂ NCH₂ C₆ H₄) appear to have structures in which the R groups are bonded to a tetranuclear mixed metal core by 2e-3c bonds.

As shown by X-ray analysis the organogold(I) complex $CpFeC_5H_4$ - $(AuPPh_3)_2 \,^{\dagger}BF_4 \,^{-}$ contains electron-deficient Au-C bonds [5]. Bridging phenyl groups are proposed for triphenylgold(I)zinc, recently reported by Van der Kerk et al. [6]. On the other hand Vaughan [7] has described the isolation of 2-pyridylgold(I) for which a trimeric structure (intermolecular Au-N coordination) with electron precise Au-C bonds is proposed.

In connection with our interest in the nature of the bonding in aryl derivatives of Group IB metals we have prepared arylgold(I) compounds containing built-in ligands.

The 1/1 reaction of 2-[(dimethylamino)methyl] phenyllithium (I) with chloro(triphenylarsme)gold(I) afforded in addition to free Ph₃ As (isolated quantitatively) an ether- and benzene-insoluble solid II. Pure 2-[(dimethylamino)methyl] phenylgold(I) (III) could not be isolated from this solid. Its formation, however, was established via the interaction of II with triphenyl-

phosphine which afforded benzene-soluble RAuPPh3 (IV).

RLi + ClAu(AsPh₃)
$$\xrightarrow{\text{Et}_2 \text{O}}$$
 [RAu/LiCl] + AsPh₃
(I) (II) \downarrow PPh₃
(R = 2-Me₂ NCH₂ C₆ H₄) RAuPPh₃
(IV)

IV as well as other arylgold(I) triphenylphosphine complexes were isolated from the 1/1 reaction of the respective organolithium compounds with bromo(triphenylphosphine)gold(I). The aryl(triphenylphosphine)gold(I) complexes IV-VIII exist in benzene as discrete monomeric species (osmometry). The compounds were identified by elemental analysis (C, H, N, Au and P), by NMR spectroscopy (correct resonance pattern) and by IR spectroscopy.

$$R'$$
 $(CH_2)_n - L_1 + BrAuPPn_3 \longrightarrow R'$
 $(CF_2)_n AuPPn_3 + L.Br$
 $(IX) - (ZIII)$

(
$$\square$$
) $n = 0$, $R' = 2 - Me_2NCH_2$; 65% yield; mp 995-100°
(\square) $n = 0$, $R' = 2 - Me_2N$; 80% yield; mp 172-174° (dec.)
(\square) $n = 0$, $R' = 2.6 - (MeO)_2$, 90% yield; mp 164-178° (dec.)
(\square) $n = 0$, $R' = 2.4.6 - (MeO)_2$, 50% yield, mp 148-150° (dec.)
(\square) $n = 1$, $R' = 2 - Me_3NCH_2$, 65% yield, mp \bowtie 90° (dec.)

Pure, uncomplexed 2-[(dimethylamino)methyl] phenylgold (III) was prepared via a novel reaction sequence:

$$R_4 Au_2 Li_2 + 2 Me_3 SnBr \rightarrow 2 Me_3 SnR + 2/n (RAu)_n + 2 LiBr$$

$$(R = 2-Me_2 NCH_2 C_6 H_4)$$

The high insolubility of III (colourless, 95 % yield; dec. at 117°) in hydrocarbon and ether solvents points to a polymeric structure. Since monovalent gold seems to prefer a digonal stereochemistry [8] this structure may involve either 2e-3c Au-C bonding without Au-N coordination or electron-precise Au-C bonding with intermolecular Au-N coordination (cf. ref. 7).

III is soluble in pyridine. Its ¹H NMR spectrum in pyridine- d_5 shows two sets of signals for the NMe and NCH₂ protons (A: δ 2.38 and 4.09 and B; 2.91 and 4.30 ppm: A/B 3.5/1). Upon addition of PPh₃ (R_nAu_n/nPPh₃ 1/1) to this solution an NMR spectrum is observed, identical to that of pure monomeric RAu-PPh₃ (IV) [δ (NCH₃) 2.28 s and δ (NCH₂) 3.90 ppm s]. This indicates the presence of different aggregates of RAu in pyridine solution. In contrast, break-down of the tetranuclear structure of R₄ Cu₄ [3a] with pyridine or PPh₃ [9] does not occur.

The synthesis by the above reaction sequence of further examples of uncomplexed $(RAu)_n$ as well as the possibility that the formation of these compounds from R_4 Au₂ Li₂ proceeds via an Au^{III}—Sn intermediate is under investigation.

$$R_2 Au^I Li + R'_3 SnX \xrightarrow{-LiX} [R_2 Au^{III}SnR'_3] \rightarrow R'_3 SnR + RAu$$
(Dimer)

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