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Preliminary communication

NOVEL ARYL-BRIDGED TETRANUCLEAR GOLD—LITHIUM AND GOLD—COPPER CLUSTER COMPOUNDS $R_4Au_2M_2$ (M = Li OR Cu)

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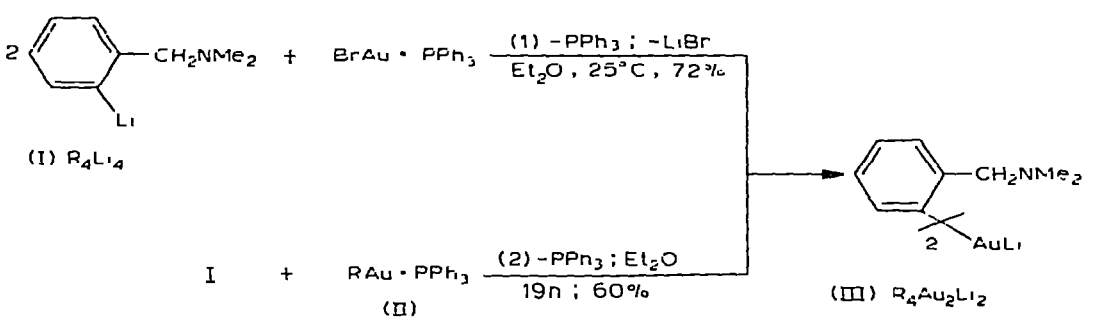
Summary

Thermostable 2-Me_2NCH_2-substituted phenylgoldlithium and goldcopper cluster compounds $R_4Au_2M_2$ have been isolated and characterized.

As part of our investigations of the influence of built-in ligands on the structure of organometal IB compounds, we have prepared novel mixed Au_2Li_2 and Au_2Cu_2 cluster compounds.

Bis{2-[(dimethylamino)methyl]phenyl}goldlithium (III) has been synthesized via route 1* as well as via route 2.



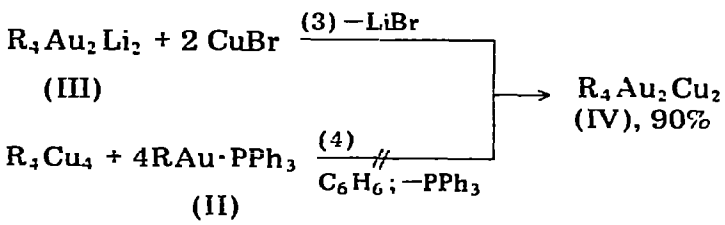
White III, which is soluble in benzene and slightly soluble in ether, exists in benzene as a discrete dimer (by ebulliometry) and thus has $R_4Au_2Li_2$ stoichiometry. As compared with lithium dimethylbis(pyridine)aurate(I) [1] (stable below 0°) $R_4Au_2Li_2$ is thermally remarkably stable (slow dec. at 170°C; fast dec. at 202-204°).

The structure of the related $R_4Cu_2Li_2$ [2] and $R_4Ag_2Li_2$ [3] (R = 2-Me_2NCH_2-

*Bis(2,6-dimethoxyphenyl)goldlithium (insoluble in hydrocarbon solvents; soluble in pyridine; 60% yield; dec. at 150°) has been prepared by the same method.

C_6H_4) compounds consists of a *trans*-M_2Li_2 core with $2e$—$3c$ bonded aryl groups* The observation that the ^{13}C and ^1H NMR** spectra of $R_4Au_2Li_2$ very closely resemble those of the corresponding copper and silver compounds indicates a similar structure for this compound, with digonal Au^I atoms (two electron-deficient Au—C bonds) and tetragonal Li atoms (two electron-deficient Li—C bonds and two Li—N coordination bonds). The absence of PPh_3 in the reaction product III is in line with the view that monovalent gold has a preference for linear two-coordination [5].

Compounds of type III, apart from being useful starting materials for the synthesis of uncomplexed $(RAu)_n$ species [6], are readily converted into other polynuclear mixed metal species. An example is the isolation of bis{2-[(dimethylamino)methyl]phenyl}goldcopper (IV) from the reaction of CuBr with $R_4Au_2Li_2$ (route 3)***.



Ochre IV (dec. at 137-139°) is revealed by ebulliometry to be dimeric in benzene, suggesting a structure consisting of a tetranuclear AuCu core with $2e$—$3c$ bonded aryl groups identical to that established for tetranuclear 2-[(dimethylamino)-methyl]phenylcopper [8]. The ^1H NMR spectrum of IV is temperature-dependent [in C_6D_6: broad signals at 25°C; at 80°C: 2.04 (s, sharp, NCH_3), 3.28 (s, broad, NCH_2), 8.0 ppm (d, broad, J 7 Hz, H_6]. This can be explained by the presence in solution of species of the type $R_4Cu_{4-n}Au_n$ (the overall stoichiometry $R_4Au_2Cu_2$ is confirmed by the analytical results) which undergo slow interaggregate exchange. A similar interaggregate exchange has been observed upon dissolving $R_4Ag_{6-n}Cu_nBr_2$ (n = 2 or 4) in benzene [9].

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*Each aryl group is bonded via carbon (C(1)) to one M (Cu or Ag) atom and to one Li atom. E.g., $R_4Ag_2Li_2$ [3] $J(^{13}C(1)—Li)$ 7.2 ± 0.2 and $J(^{13}C(1)—^{107}Ag)$ 118.3 ± 0.8, $J(^{13}C(1)—^{109}Ag)$ 136.0 ± 0.8 Hz. Bridging phenyl groups are proposed to occur in recently isolated triphenylgoldzinc [4].

**The low intensity ^{13}C resonance at 174.4 ppm (in C_6D_6) is assigned to C(1) (bridging carbon atom). Since the signal is somewhat broadened the multiplicity could not be established. Only one ^1H resonance pattern is observed for all aromatic protons (8.52 ppm, d of d, J 7 Hz, H_6). The CH_2 protons appear at room temperature as an AB pattern (2.40 and 4.30 ppm; $J \approx 12$ Hz; coalescence at about 80°).

***Reaction of $RAu \cdot PPh_3$ [6] with R_4Cu_4 [7] (route 4) does not occur.

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