

### 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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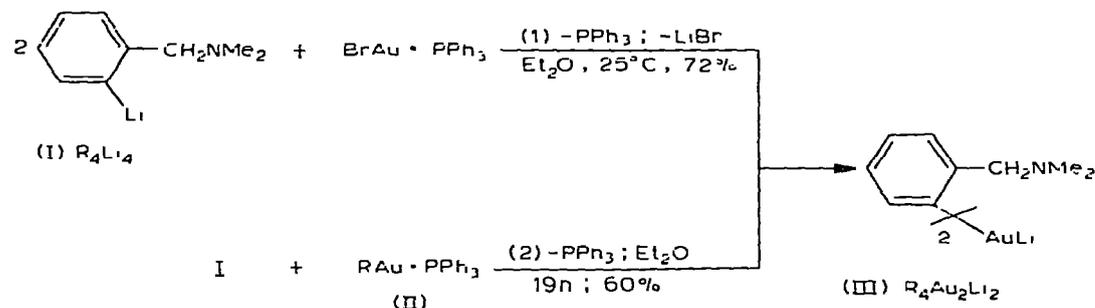
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### Summary

Thermostable 2-Me<sub>2</sub>NCH<sub>2</sub>-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.



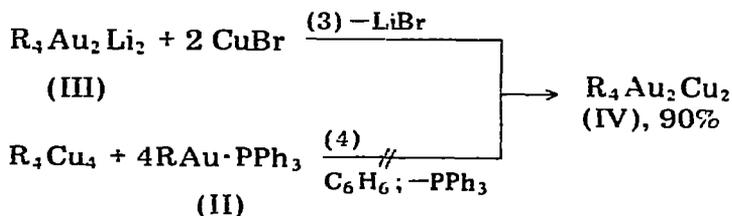
White III, which is soluble in benzene and slightly soluble in ether, exists in benzene as a discrete dimer (by ebulliometry) and thus has  $R_4Au_2Li_2$  stoichiometry. As compared with lithium dimethylbis(pyridine)aurate(I) [1] (stable below 0°)  $R_4Au_2Li_2$  is thermally remarkably stable (slow 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] ( $R = 2\text{-Me}_2\text{NCH}_2\text{-}$

\* 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<sup>\*</sup>. The observation that the  $^{13}C$  and  $^1H$  NMR<sup>\*\*</sup> 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)<sup>\*\*\*</sup>.



Ochre IV (dec. at  $137-139^\circ$ ) 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  $25^\circ C$ ; at  $80^\circ C$ : 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  $R_4Cu_4-nAu_n$  (the overall stoichiometry  $R_4Au_2Cu_2$  is confirmed by the analytical results) which undergo slow inter-aggregate exchange. A similar interaggregate exchange has been observed upon dissolving  $R_4Ag_6-nCu_nBr_2$  ( $n = 2$  or  $4$ ) in benzene [9].

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## References

- 1 A. Tamaki and J.K. Kochi, J. Chem. Soc., Dalton Trans., (1973) 2620.
- 2 G. van Koten and J.G. Noltes, J. Chem. Soc., Chem. Commun., (1972) 940.
- 3 A.J. Leusink, G. van Koten, J.W. Marsman and J.G. Noltes, J. Organometal. Chem., 55 (1973) 419.

<sup>\*</sup> 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]  $J(^{13}C(1)-Li)$   $7.2 \pm 0.2$  and  $J(^{13}C(1)-^{107}Ag)$   $118.3 \pm 0.8$ ,  $J(^{13}C(1)-^{109}Ag)$   $136.0 \pm 0.8$  Hz. Bridging phenyl groups are proposed to occur in recently isolated triphenylgoldzinc [4].

<sup>\*\*</sup> 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  $80^\circ$ ).

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

- 4 P.W.J. de Graaf, J. Boersma and G.J.M. van der Kerk, *J. Organometal. Chem.*, 78 (1974) C19.
- 5 F.A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 3rd ed., Interscience, London, 1972, p.1053.
- 6 G. van Koten and J.G. Noltes, *J. Organometal. Chem.*, 80 (1974) C56.
- 7 G. van Koten, A.J. Leusink and J.G. Noltes, *Chem. Commun.*, (1970) 1107.
- 8 G. van Koten and J.G. Noltes, *J. Organometal. Chem.*, 84 (1975) 129.
- 9 A.J. Leusink, G. van Koten and J.G. Noltes, *J. Organometal. Chem.*, 56 (1973) 379.