

Preliminary communication

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

GERARD VAN KOTEN and JAN G. NOLTES

Institute for Organic Chemistry TNO, Utrecht (The Netherlands)

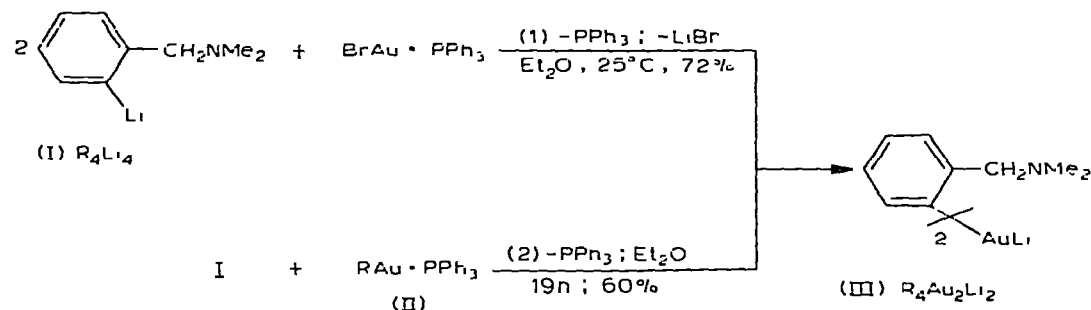
(Received October 18th, 1974)

Summary

Thermostable 2-Me₂NCH₂-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.



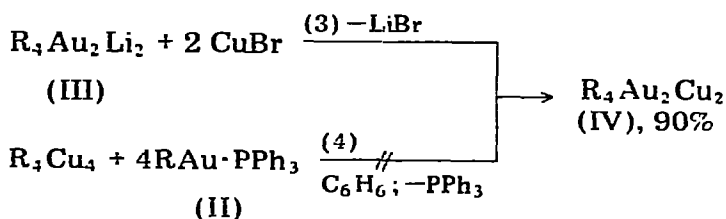
White III, which is soluble in benzene and slightly soluble in ether, exists in benzene as a discrete dimer (by ebulliometry) and thus has $R_4Au_2Li_2$ stoichiometry. As compared with lithium dimethylbis(pyridine)aurate(I) [1] (stable below 0°) $R_4Au_2Li_2$ is thermally remarkably stable (slow dec. 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-Me₂NCH₂-

* 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 $137-139^\circ$) 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].

Thanks are due to Mr. C.A. Schaap for able experimental assistance.

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.

^{*} 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.

- 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.