Trimeric Gold(I) Derivatives of Pyrazoles: a Novel Type of Inorganic Ring

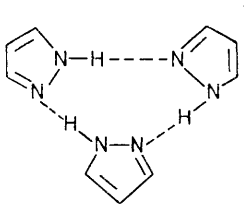
By FLAVIO BONATI,* GIOVANNI MINGHETTI, and GUIDO BANDITELLI
(*Istituto di Chimica Generale dell'Universitá di Milano, Laboratorio CNR, via Venezian* 21 20133, *Milano, Italy*)

Summary Reaction of methanolic KOH with Me_2SAuCl and 1-unsubstituted pyrazoles gives *N*-pyrazolylgold(I) derivatives, for which a novel type of nine-membered inorganic ring is suggested.

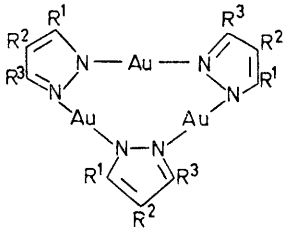
THERE is convincing evidence[1] for the existence of stable trimers of pyrazole and 3,5-dimethylpyrazole [*e.g.* structure (A)]. If a monovalent and usually two-co-ordinate metal ion (*e.g.* Au^I) could replace the bridging hydrogen atom, a novel type of inorganic, nine-membered ring structure should be obtained. We therefore examined the products of reaction (1), where HY is a 1-unsubstituted pyrazole.

$$HY + KOH + Me_2SAuCl \xrightarrow{MeOH} AuY + KCl + H_2O + Me_2S \quad (1)$$

The white compounds which precipitated were crystallized† from hot benzene or pyridine. The pure compounds are stable to air, light, and heat; they are only slightly soluble in most organic solvents. Their i.r. spectra show no evidence of an N–H group, and the ^1H n.m.r. spectrum of compound (III), shows a pyrazole 4-H signal (*ca.* τ 3·8 in C_6D_6). These facts and the isolation of the derivative (IV) of 3,5-dimethyl-4-ethylpyrazole show that the pyrazole ring is *N*-substituted. Molecular weight determinations show that the compounds are trimeric both in the vapour phase [parent ion was detected for (I), (II), and (IV)] and in chloroform solution [*M* 996 for (III) calc. 1062; 1020 for (IV), calc. 960; 0·3% w/w]. We suggest structures (I)—(IV) for these compounds since they satisfy the requirements of a trimeric, nine-membered ring structure. The n.m.r. spectrum (C_6D_6) of (III) showed the presence of stereoisomers,



(A)



(I) R^1 = H, R^2 = H, R^3 = H
(II) R^1 = Me, R^2 = H, R^3 = Me
(III) R^1 = Me, R^2 = H, R^3 = Ph
(IV) R^1 = Me, R^2 = Et, R^3 = Me

as would be expected for a compound derived from an asymmetric pyrazole.

(*Received*, 26*th October* 1973; *Com.* 1478.)

† Satisfactory analytical, i.r. and n.m.r. data were obtained for all the compounds.

[1] A. Albert, 'Heterocyclic Chemistry,' The Athlone Press, London, 1968; D. M. W. Anderson, J. L. Duncan, and F. J. C. Rossotti, *J. Chem. Soc.*, 1961, 140.