

Preliminary communication

TRIPHENYLGOLDZINC

P.W.J. DE GRAAF, J. BOERSMA and G.J.M. VAN DER KERK

Laboratory for Organic Chemistry, State University, Utrecht (The Netherlands)

(Received August 2nd, 1974)

Summary

Triphenylgoldzinc has been prepared by treatment of diphenylzinc with either AuCl_3 or $\text{Au}(\text{CO})\text{Cl}$; it is thought to have a dimeric structure containing phenyl bridges between Zn and Au atoms.

Some new ways of synthesizing arylgold compounds have recently been reported. Liddle and Parkin [1] prepared mono-, di- and tri-arylgold(III) compounds from arylmercury or arylcadmium compounds and gold trichloride and Braunstein [2] obtained monoarylgold(III) salts from aryl hydrazines. Nesmeyanov et al. [3] have described some new organogold compounds containing the ferrocenyl moiety.

We have found that the reaction of diphenylzinc with gold trichloride affords an orange-red compound which analyses correctly for $(\text{C}_6\text{H}_5)_3\text{AuZn}$ and which is a remarkably thermally stable compound. We propose structure I for the compound on the basis of the following considerations:

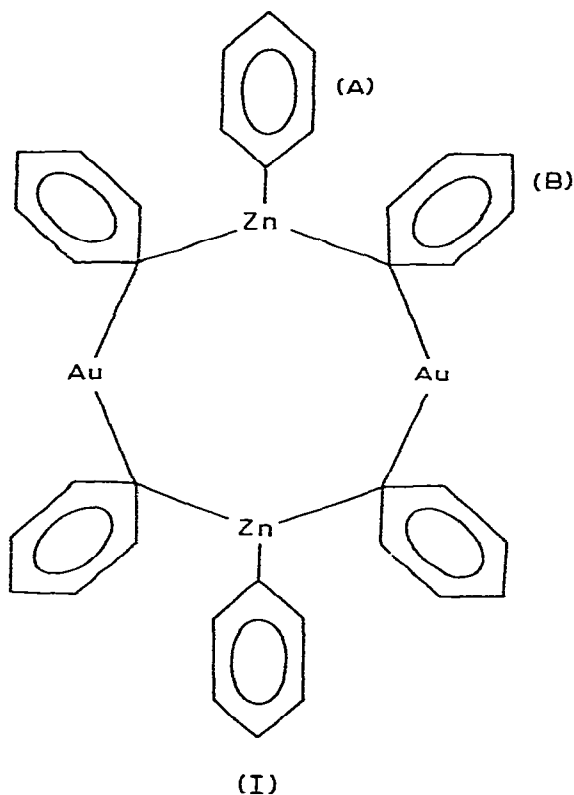
(a) Cryoscopy showed the compound to be dimeric in benzene at various concentrations.

(b) ^1H NMR spectroscopy* at room temperature in CS_2 ** proved the existence of two kinds of phenyl groups in a 1/2 ratio, A at 7.42 ppm (singlet) and B at 8.20 ppm (*ortho* H atoms, multiplet) and 7.84 ppm (other H atoms, multiplet), respectively. Below -25° the signal of A is split while the signals of B are not, suggesting for A the possible presence of two different conformations.

(c) In the proton noise-decoupled ^{13}C NMR spectrum one can distinguish one set of 4 signals which is almost identical with that given by pure diphenylzinc, and which thus belongs to phenyl groups exclusively bound to zinc (A), and a second set of 4 signals which must be assigned to the bridging phenyl groups B. The intensity of the latter set is about twice the intensity of the former.

*All chemical shifts are δ values relative to TMS.

**Under our experimental conditions CS_2 does not react with either diphenylzinc or triphenylgoldzinc.



(d) Compound I clearly contains gold in the monovalent state. In fact oxidative addition of iodomethane furnishes a greenish compound, the constitution of which is at present under investigation.

The same compound I was obtained starting from $\text{Au}(\text{CO})\text{Cl}$ and a three-fold excess of diphenylzinc. When this reaction was carried out using a 1/1 ratio of the reactants a cream-coloured compound II was isolated which analysed correctly for $(\text{C}_6\text{H}_5)_2\text{AuZnCl}$. The ^{13}C NMR spectrum in CS_2 shows only 4 signals at positions corresponding to those assigned to the bridging phenyl groups in I. Presumably II has a structure somewhat similar to I in which the phenyl groups attached exclusively to zinc (A) are replaced by chlorine.

In structure I the zinc is coordinatively unsaturated. It is likely that in compound II coordinative saturation of the zinc will be achieved by means of two-fold zinc-chlorine coordination. Unfortunately, the insolubility of II in benzene prevented a cryoscopic molecular weight determination.

There is one remarkable difference in chemical behaviour between I and II: the orange-coloured compound I is extremely sensitive to moisture, whereas the cream-coloured compound II is rather stable in air. This may be attributed to the absence of ordinary zinc-carbon bonds in II. The bridging phenyls are obviously less sensitive to hydrolysis.

Bridging phenyl groups as we postulate are not unusual for the coinage metals. Van Koten et al. [4, 5] found these to occur in arylcopper and arylsilver compounds, and Andrianov [6] gives an example in a related ferrocenylgold compound.

Compounds of the types I and II can also be obtained from substituted diarylzinc compounds; e.g. ditolylzinc gives similar reactions. We are at present extending this series further.

Acknowledgement

This investigation was supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

References

- 1 K.S. Liddle and C. Parkin, Abstr. Paper VIth Int. Conf. Organometal. Chem., Amherst 1973, no. 213.
- 2 P. Braunstein, J. Chem. Soc., Chem. Commun., (1973) 851.
- 3 A.N. Nesmeyanov, E.G. Perevalova, K.I. Grandberg, D.A. Lemenovskii, T.V. Bankova and O.B. Afanasova, J. Organometal. Chem., 65 (1973) 131.
- 4 J.M. Guss, R. Mason, I. Sotofte, G. van Koten and J.G. Noltes, J. Chem. Soc., Chem. Commun., (1972) 446.
- 5 A.J. Leusink, G. van Koten, J.W. Marsman and J.G. Noltes, J. Organometal. Chem., 55 (1973) 419.
- 6 V.G. Andrianov, Yu.T. Struchkov and E.R. Rossinskaja, J. Chem. Soc., Chem. Commun., (1973) 338.