

### Preliminary communication

## FERROCENYL COPPER

A.N. NESMEYANOV, N.N. SEDOVA, V.A. SAZONOVA\*, and S.K. MOISEEV

*Institute of Organoelement Compounds, Academy of Sciences of the USSR, Vavilov St. 28, Moscow 117813 (U.S.S.R.)*

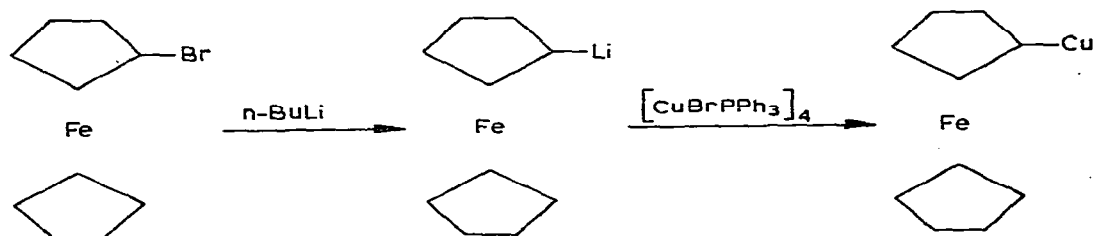
(Received October 25th, 1979)

### Summary

Ferrocenylcopper is obtained by the interaction of ferrocenyllithium with  $[\text{CuBrPPh}_3]_4$ . The reactions of the organocopper compound with iodobenzene and benzoyl chloride are studied.

The first representative of ferrocene organocopper derivatives, 2-copper(dimethylaminomethyl)ferrocene [1] obtained by the action of the copper iodide complex with dimethylaminomethylferrocene on 2-lithium(dimethylaminomethyl)ferrocene, is a crystalline substance stable in air for a long time. X-ray structural study [2] shows that it has cluster tetrameric structure with bridging ferrocenyl groups. 2-Silver(dimethylaminomethyl)ferrocene obtained under similar conditions has an analogous structure [3,4]. In all other stable organo-silver ferrocene compounds, i.e. 1-(2-chloroferrocenyl)silver [5], 1-(1'-chloroferrocenyl)silver [6], and 1-(1'-bromoferrocenyl)silver [7], there are substituents in the ferrocenyl nucleus which apparently stabilise the C—Ag bond at the expense of Ag...halogen coordination. Organocopper and organosilver ferrocene compounds without substituents capable of stabilising metal—carbon bonds in the ferrocene nucleus have not been found so far.

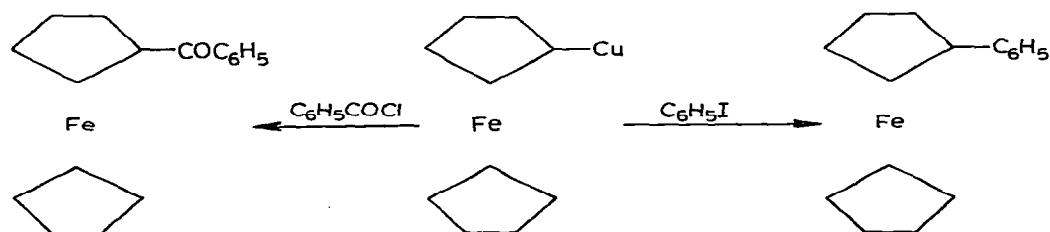
Ferrocenylcopper was obtained with a 72% yield by the action of  $[\text{CuBrPPh}_3]_4$  in benzene solution on an ether solution of ferrocenyllithium obtained from bromoferrocene and n-butyllithium.



Cleavage of the Cu—ligand bond was observed on formation of organocopper compound in this case and free triphenylphosphine was found in the reaction mixture after isolation of ferrocenylcopper by thin-layer chromatography.

Ferrocenylcopper is an orange-colored substance stable in air for a short period of time and insoluble in the majority of organic solvents, the latter fact testifying to the polymeric structure of the substance. When left in air ferrocenylcopper decomposes with the formation of ferrocene and ferrocenyl. On heating the compound to a temperature higher than 120°C in inert atmosphere the same products are formed.

Ferrocenylcopper readily reacts with acid halides forming the corresponding acyl derivatives of ferrocene. Thus, benzoylferrocene with a 56% yield and traces of ferrocene and diferrocenyl are formed on stirring a benzene suspension with benzoyl chloride for a short time under an inert atmosphere.



The formation of diferrocenyl apparently occurs in competition with the decomposition of the benzene suspension of ferrocenylcopper by traces of oxygen. Thus, when this reaction takes place in air the yield of benzoylferrocene goes down to 33% while the yield of diferrocenyl and ferrocene goes up to 54% and 13% respectively.

Aryl halides react with organocopper compounds of ferrocene [1,8] and cymantrene [9] with substitution of copper by an aryl group. Phenylferrocene with 70% yield and traces of ferrocene and diferrocenyl are formed on heating ferrocenylcopper with iodobenzene in an inert atmosphere at 130°C. The study of the structure and properties of ferrocenylcopper continues in this laboratory.

## Experimental

**Ferrocenylcopper.** 2 ml of (0.95 M) n-butyllithium solution in hexane are added to an ether solution of 0.5 g of bromoferrocene at  $-70^{\circ}\text{C}$ . A solution of 0.77 g of  $[\text{CuBrPPh}_3]_4$  in benzene is added to the mixture at  $0^{\circ}\text{C}$  and the reaction mixture is kept for 1 h at  $25^{\circ}\text{C}$ . The precipitate is washed under argon with absolute ether, water, again ether and dried in a vacuum-desiccator. 0.34 g (72% yield) of ferrocenylcopper is obtained as an amorphous powder. Found: C, 48.12; H, 3.90; Fe, 21.78; Cu, 26.07.  $\text{C}_{10}\text{H}_5\text{FeCu}$  calcd.: C, 48.29; H, 3.65; Fe, 22.46; Cu, 25.56%.

**Phenylferrocene.** Several drops of iodobenzene are added to 0.15 g of freshly prepared ferrocenylcopper. The mixture is heated in an argon flow at  $130^{\circ}\text{C}$  for 1 h and then treated with benzene. The benzene solution is filtered and the solvent evaporated off. The remainder is separated on a thin layer of  $\text{Al}_2\text{O}_3$  with petroleum ether. 0.11 g of phenylferrocene (70% yield), m.p.  $109\text{--}110^{\circ}\text{C}$

(literature data m.p. 110–111°C [10]) is obtained.

*Interaction of ferrocenylcopper with benzoyl chloride.* a) 0.25 ml of benzoyl chloride are added to benzene suspension of 0.2 g of ferrocenylcopper. The mixture is stirred in argon flow at 25°C for 1 h. The precipitate is filtered, organic solution is washed by water and ammonia solution, solvent is evaporated. The remainder is separated on a thin layer of Al<sub>2</sub>O<sub>3</sub> with a petroleum ether–benzene mixture (4:1). 0.14 g (56% of theoretical) of benzoylferrocene, m.p. 109–110°C (literature data 108–108.3°C [11]) and traces of ferrocene and diferrocenyl are obtained.

b) Similarly 0.08 g (33% yield) of benzoylferrocene, 0.08 g (54% yield) of diferrocenyl and 0.02 g of ferrocenyl (13% yield) were obtained from 0.2 g of ferrocenylcopper and 0.25 ml of benzoyl chloride by reaction in air.

## References

- 1 A.N. Nesmeyanov, V.A. Sazonova, N.N. Sedova, Yu.V. Volgin and O.V. Dudukina, Dokl. Akad. Nauk SSSR, 226 (1976) 1092.
- 2 A.N. Nesmeyanov, Yu.T. Struchkov, N.N. Sedova, V.G. Andrianov, Yu.V. Volgin and V.A. Sazonova, J. Organometal. Chem., 137 (1977) 217.
- 3 A.N. Nesmeyanov, V.A. Sazonova, N.N. Sedova and E.N. Stakheeva, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 2354.
- 4 A.N. Nesmeyanov, N.N. Sedova, Yu.T. Struchkov, V.G. Andrianov, E.N. Stakheeva and V.A. Sazonova, J. Organometal. Chem., 153 (1978) 115.
- 5 A.N. Nesmeyanov, V.A. Sazonova and N.S. Sazonova, Dokl. Akad. Nauk SSSR, 176 (1967) 598.
- 6 A.N. Nesmeyanov, V.A. Sazonova, N.S. Sazonova and V.N. Plyukhina, Dokl. Akad. Nauk SSSR, 177 (1967) 1352.
- 7 A.N. Nesmeyanov, N.S. Sazonova, V.A. Sazonova and L.M. Meskhi, Izv. Akad. Nauk SSSR, Ser. Khim., (1969) 1827.
- 8 A.N. Nesmeyanov, N.N. Sedova, Yu.V. Volgin and V.A. Sazonova, Dokl. Akad. Nauk, 228 (1976) 1347.
- 9 A.N. Nesmeyanov, V.A. Sazonova, N.N. Sedova, L.S. Borodina and Yu.V. Volgin, Dokl. Akad. Nauk SSSR, 213 (1973) 1099.
- 10 G.D. Broadhead and P.L. Pauson, J. Chem. Soc., (1956) 367.
- 11 M.D. Rausch, M. Vogel and H. Rosenberg, J. Org. Chem., 22 (1957) 900.