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Preliminary communication

SYNTHESIS AND PROPERTIES OF 1,1'-FERROCENYLENEDICOPPER

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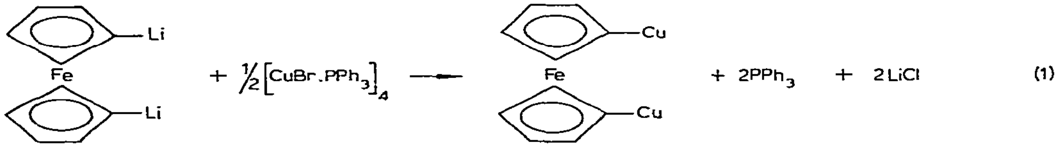
Summary

1,1'-Ferrocenylenedicopper is obtained by the action of $[CuBr \cdot PPh_3]_4$ on 1,1'-ferrocenylenedilithium; thermal decomposition and interaction with $CuCl_2$ has been studied.

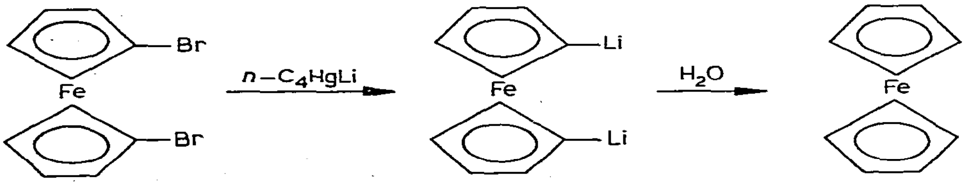
We have recently reported the synthesis of ferrocenylcopper [1] and ferrocenylsilver [2]. These compounds are fairly stable. The possibility of the existence and the properties of a ferrocene derivative containing 2 metal atoms in one ferrocene radical is of considerable importance for further study of the properties of organocopper and organosilver metallocene derivatives.

This paper describes the synthesis and properties of 1,1'-ferrocenylenedicopper which is formed in the reaction of 1.1'-ferrocenylenedilithium with phosphine complexes of copper salts (eq. 1).



(1)

Initially 1,1'-ferrocenylenedilithium is obtained by metallation of 1,1'-dibromoferrocene by n-butyllithium at low temperature, i.e. by a similar method as used in the synthesis of ferrocenyllithium from ferrocene halides [3].

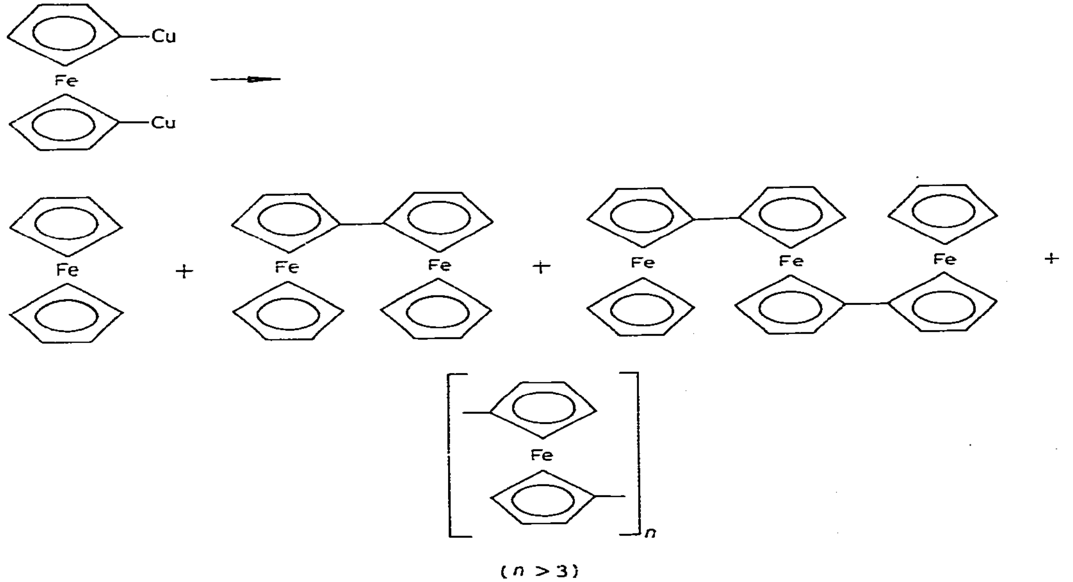


(2)

The metallation process leading to quantitative formation of 1,1′-ferrocenylenedilithium is confirmed by decomposition of the reaction mixture in water (eq. 2). The PMR spectrum of the reaction products shows a singlet only which belongs to protons of unsubstituted ferrocene.

The formation of 1,1′-ferrocenylenedicopper, as well as with ferrocenylcopper, and -silver [2], 2-copper-(*N,N*-dimethylaminomethyl)ferrocene [4], 2-copper- and 2-silver-(methoxy)ferrocene [5], exhibits the cleavage of metal—ligand bonds leading to the formation of free triphenylphosphine in the reaction mixture which is identified as iodomethylate (91% yield of 1,1′-ferrocenylenedicopper).

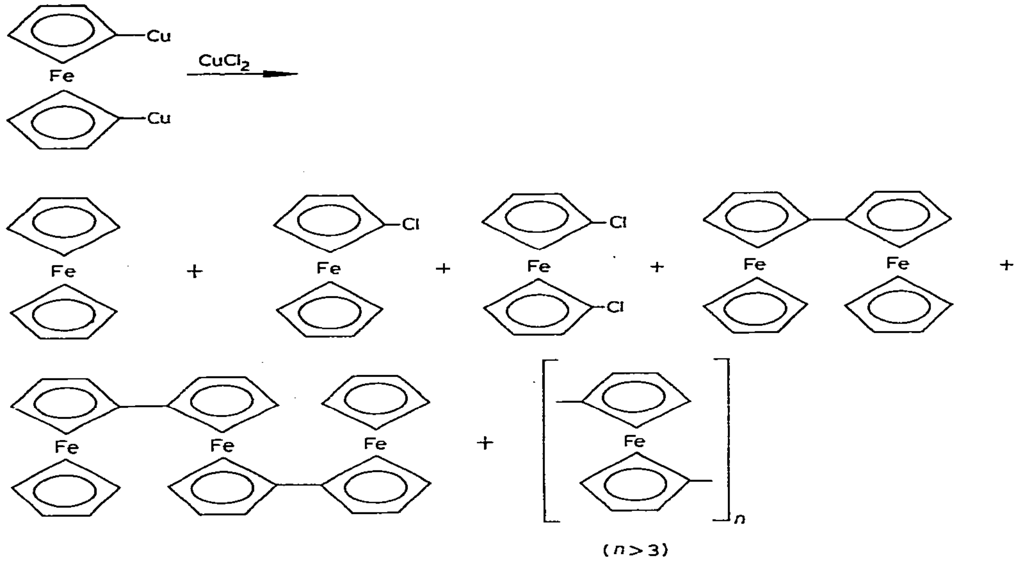
1,1′-Ferrocenylenedicopper is a red-orange solid, which is insoluble in common organic solvents. The compound remains unchanged for 24 h in vacuum, while in air it decomposes slowly after 1.5—2 h. Decomposition in air is complete after several days with formation of ferrocene, diferrocene, 1,1′-terferrocene and polyferrocenes (eq. 3).



(3)

1,1′-Ferrocenylenedicopper is thermally stable. On heating (4°C/min) in a sealed capillary the substance decomposes at 136°C, with formation of ferrocene, diferrocene and 1,1′-terferrocene (identified by TLC with reference spots). Polyferrocenyls formed were not studied in detail.

As we have shown in ref. 2, the action of cupric chloride on organocopper- and organosilver-ferrocene compounds leads to the exchange of copper or silver atoms for halogen and to the coupling of ferrocenyl radicals besides substitution of metal for hydrogen. Cupric chloride reacts similarly with 2-(dimethylaminomethyl)phenylcopper [6]. Similar behaviour is also observed for 1,1′-ferrocenylenedicopper, thus, the interaction of 1,1′-ferrocenylenedicopper with $CuCl_2$ yielded all the expected reaction products (eq. 4), with 1,1′-dichloroferrocene, 1,1′-terferrocene and polyferrocene as the main reaction products.



(4)

Experimental

All experiments were carried out under dry argon.

1,1′-Ferrocenylenedicopper. A solution of 1,1′-ferrocenylenedilithium (0.5 g 1,1′-dibromoferrocene and 2.00 ml 1.45 *N* n-butyllithium in hexane) in 20 ml of dry ether was added with stirring to a solution of 0.85 g of $[CuBr \cdot PPh_3]_4$ in 80 ml of dry benzene. The reaction mixture immediately became dark-red. An orange-red precipitate appeared after 5—10 min. The mixture was stirred for another 1.5—2 h, after which the solution was decanted, the precipitate filtered, washed with dry ether, water, ether (all operations were carried out under dry argon), and finally dried in a vacuum-desiccator over $CaCl_2$. 0.31 g of product was obtained (yield 95%, based on $[CuBr \cdot PPh_3]_4$, decomp. p. 136°C, in a sealed capillary). A halide test was negative. Found: C, 38.93; H, 3.13. $C_{10}H_8Cu_2Fe$ calcd.: C, 38.61; H, 2.59%.

The organic solvents were mixed, washed with water, treated by 2 ml of methyl iodide and left over during the night. The precipitate formed was filtered off, washed with ether and dried over $CaCl_2$. 0.73 g of triphenylphosphine iodomethylate was obtained (91% based on 1,1′-ferrocenylenedicopper isolated), m.p. 185—190°C (after reprecipitation from methylene chloride into ether, lit. m.p. 183—185°C [7]).

Metallation of 1,1′-dibromoferrocene. 0.78 ml 1.50 *N* n-butyllithium in hexane was added to 0.2 g 1,1′-dibromoferrocene in 20 ml of dry ether and cooled to —70°C. Then the temperature of the reaction mixture was raised to 10°C and 0.5 ml water was added. The organic layer was separated, washed with water, and the solvent eliminated. The remainder was dried in a vacuum desiccator over $CaCl_2$. The PMR spectrum of the reaction product (60 MHz, CCl_4, TMS-internal standard) showed a singlet at δ 4.06 ppm, which belonged to protons of unsubstituted ferrocene, 0.11 g ferrocene was obtained (quant. yield), m.p. 172—173°C (from hexane).

Reaction of 1,1′-ferrocenylenedicopper with $CuCl_2$. 0.6 g anhydrous $CuCl_2$

in 5 ml ethanol was added to a suspension of 0.31 g 1,1'-ferrocenylenedicopper in 5 ml benzene. After stirring for 3 h at room temperature the reaction mixture was treated with 10% ammonia solution and stirred for 30 min. The organic layer was separated, washed with water and the solvent eliminated. The remainder was chromatographed (TLC, Al_2O_3, petroleum ether/ether mixture (13/1)). A mixture was obtained, consisting of 0.02 g of ferrocene, chloroferrocene and 1,1'-dichloroferrocene in the ratio 4/7/3 according to the PMR spectrum (100 MHz in CCl_4; TMS-internal standard. δ (ppm): 3.96 (m, 2H, C_5H_4), 4.16 (s, 5H, C_5H_5), 4.30 (m, 2H, C_5H_4 of chloroferrocene); 4.06 (4H, $2C_5H_4$ of 1,1'-dichloroferrocene and 10H, $2C_5H_5$ of ferrocene), 4.35 (4H, $2C_5H_4$ of 1,1'-dichloroferrocene)); 0.01 g (5% based on 1,1'-ferrocenylenedicopper) of diferrocene, m.p. 239—240°C (decomp.) (lit. m.p. 239—240°C, decomp. [8]); 0.02 g (11%) of 1,1'-terferrocene, m.p. 212—214.5°C (lit. m.p. 212.5—214.5°C [9]) and 0.07 g (38%) of polyferrocenes.

Thermal decomposition of 1,1'-ferrocenylenedicopper. 1,1'-Ferrocenylenedicopper wetted by xylene was heated for 2 h at 130—135°C. The reaction products after cooling to room temperature were extracted by benzene (5 × 10 ml) and then by trichloromethane (3 × 10 ml). Trichloromethane extracts contained polyferrocenes only. The benzene fractions were mixed, the benzene evaporated, the remainder chromatographed (TLC, Al_2O_3, petroleum ether/ether mixture (13/1)). Ferrocene, diferrocene and 1,1'-terferrocene were eluted and identified by TLC with reference spots.

References

1 A.N. Nesmeyanov, N.N. Sedova, V.A. Sazonova and S.K. Moiseev, J. Organometal. Chem., 185 (1980) C6.
2 A.N. Nesmeyanov, V.A. Sazonova, N.N. Sedova and S.K. Moiseev, Dokl. Akad. Nauk SSSR, 252 (1980) 361.
3 F.L. Hedberg and H. Rosenberg, Tetrahedron Lett., 46 (1969) 4011.
4 A.N. Nesmeyanov, V.A. Sazonova, N.N. Sedova, Yu.V. Volgin and O.V. Dudukina, Dokl. Akad. Nauk SSSR, 226 (1976) 1092.
5 A.N. Nesmeyanov, N.N. Sedova, S.K. Moiseev and V.A. Sazonova, Dokl. Akad. Nauk SSSR, 256 (1981) 98.
6 G. van Koten and J.G. Noltes, J. Organometal. Chem., 84 (1975) 419.
7 G. Wittig and G. Geissler, Ann., 580 (1953) 44.
8 M.D. Rausch, J. Org. Chem., 26 (1961) 1802.
9 A.N. Nesmeyanov, V.N. Dorzd, V.A. Sazonova, V.I. Romanenko, A.K. Prokofiev and L.A. Nikonova, Izv. Akad. Nauk SSSR, Ser. Khim., (1963) 667.