BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 812—815 (1971)

Reactions of Haloferrocenes. V.[1] The Formation of Ferrocenyltriphenylphosphonium Perchlorate

Masaru Sato,[2] Izumi Motoyama, and Kazuo Hata
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo

(Received September 5, 1970)

The reaction of haloferrocene with tetrakis(acetonitrilo)copper(I) perchlorate in nitromethane gave a 35% yield of biferrocenyl. The addition of triphenylphosphine to the reaction system causes a remarkable change in the reaction and gives ferrocenyltriphenylphosphonium perchlorate in a good yield. The scope of the formation of the quaternary salt was investigated in comparison with the corresponding reactions in the benzene series. It was found that the ligands coordinated in the intermediate copper(I) complex strongly affect the reaction. The mechanism of the formation of ferrocenyltriphenylphosphonium salt is also discussed.

Haloferrocenes are more reactive in the reactions involving metallic copper or copper(I) salt than is halobenzene. For example, the Ullmann coupling reaction of iodoferrocene takes place at 60°C,[3] and ferrocenecarbonitrile is obtained upon heating bromo- or chloroferrocene with copper(I) cyanide at 140°C.[4] It was also found that haloferrocenes reacted easily with various copper(I) salts in boiling pyridine to give substituted ferrocenes,[5–7] and that the condensation reactions of haloferrocenes with various kinds of car-

---

[1] Part IV: M. Sato, I. Motoyama, and K. Hata, This Bulletin, **44**, 808 (1971).

[2] Present address: Department of Chemistry, Saitama University, Urawa, Saitama.

[3] M. D. Rausch, *J. Org. Chem.*, **26**, 1802 (1961).

[4] A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Chem. Ber.*, **93**, 2717 (1960).

[5] M. Sato, T. Ito, I. Motoyama, K. Watanabe, and K. Hata, This Bulletin, **42**, 1976 (1969).

[6] M. Sato, I. Motoyama, and K. Hata, *ibid.*, **43**, 1860 (1970).

[7] M. Sato, I. Motoyama, and K. Hata, *ibid.*, **43**, 2213 (1970).

boxylic acids easily took place in the presence of copper(I) oxide in boiling pyridine to give the corresponding ferrocenyl ester.[1] On the other hand, it is well known that similar reactions of the corresponding benzene derivatives occur only under more severe conditions.

In previous papers[5,6] it was suggested that the substitution reactions of haloferrocenes in the presence of copper(I) salts proceed through a ligand-exchange reaction within an intermediate copper(I) complex. From this point of view, it was supposed that if a copper(I) complex of a different type, in which a linkage between the metal and the ligand has no covalent character, is employed instead of the copper(I) salts used in the previous experiments, the exchange reaction will be prohibited and that the coupling reaction of haloferrocene will occur instead, even at a lower temperature. On the other hand, since such a copper(I) complex probably dissolves in a polar solvent to give a homogeneous solution, the reaction using it is expected to be advantageous for studying the reaction mechanism.

Results

In the present study, tetrakis(acetonitrilo)copper(I) perchlorate[8] (**1**) was used for the reaction. It has been reported[8,9] that the nature of the bonding between copper and perchlorate in this complex is entirely ionic in a polar solvent. When bromoferrocene was heated at 45°C for 72 hr with an equimolar amount of the complex **1** in nitromethane, biferrocenyl was obtained in a 35% yield, and 45.3% of bromoferrocene was recovered after the reaction. These results show that the copper(I) complex effects a Ullmann-type aryl-coupling reaction. However, the yield of the coupling product was too low as compared with that of a normal Ullmann reaction, in which iodoferrocene is coupled at 60°C to afford biferrocenyl quantitatively.[3] Thereupon, with a view to modifying the character of the complex in order to produce an increased yield of biferrocenyl, triphenylphosphine was added to the reaction mixture. Unexpectedly, however, when iodoferrocene was heated with triphenylphosphine in the presence of tetrakis(acetonitrilo)copper(I) perchlorate (**1**) in nitromethane, ferrocenyltriphenylphosphonium perchlorate (**2**) was obtained in a good yield. Furthermore, this reaction took place at a surprisingly low temperature (45°C), although never at room temperature. Bromoferrocene also reacted in a similar way, but the product was obtained only in a lower yield. These results are summarized in Table 1.

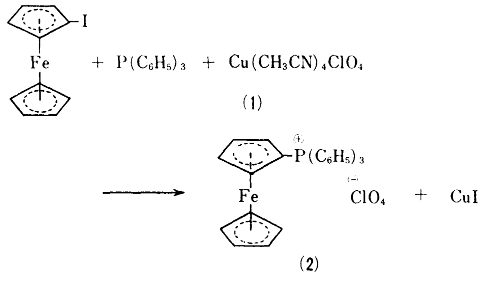


Table 1. The formation of ferrocenyltriphenylphosphonium perchlorate

Haloferrocene	Reaction temp. (°C)	Reaction time (hr)	Recovery of haloferrocene (%)	Yield (%)
FcI	44.5	15.5	35.8	61.4
FcI	101	6	14.4	80.8
FcBr	44.5	15	58.2	36.1

A reaction of this type is known also in the benzene series and is utilized as a synthetic method of aryltriphenylphosphonium salts. The reaction is generally catalyzed by anhydrous metal halide, such as aluminum chloride,[10] cobalt(II) or nickel(II) halide,[11,12] and copper(I) chloride.[13] For instance, when a substituted bromobenzene is treated with triphenylphosphine in the presence of cobalt(II) chloride or nickel(II) bromide, the corresponding aryltriphenylphosphonium bromide is obtained in a high yield, but the reaction does not occur at temperatures below 160°C.[11]

In these reactions giving quaternary phosphonium salts, haloferrocene is much more reactive than halobenzene, much as in other copper(I) salt-participating reactions. It is noticeable that the halogen atom in haloferrocene transfers to the copper(I) complex, finally giving copper(I) halide, whereas that in halobenzene moves into the phosphonium salt without coordinating to the coexisting metal halide.

As had been reported in a previous paper,[6] when the reaction of bromoferrocene with copper(I) chloride in the presence of pyridine was carried out in nitromethane, chloroferrocene was obtained. A similar reaction was attempted in the presence of triphenylphosphine instead of pyridine, but it was found that neither ferrocenylphosphonium salt nor chloroferrocene was produced. The corresponding reaction of 4-bromobiphenyl with triphenylphosphine in the presence of copper(I) chloride has been known to give 4-biphenylyltriphenylphosphonium bromide.[13]

Thus, the formation of ferrocenylphosphonium salt from iodoferrocene and triphenylphosphine was found to necessitate the presence of tetrakis(acetonitrilo)-

Table 2. The influence of the variation in molar ratio

Exp. No.	Molar ratio			Recovery of FcI (%)	Yield of phosphonium salt (%)
	FcI	$P(C_6H_5)_3$	$Cu(CH_3CN)_4ClO_4$		
1	1	1	1	35.8	61.4
2	1	2	1	64.6	6.5
3	1	4	1	86.5	—
4	1	1	0.2	96.3	—

---

[8] P. Hemmerich and C. Sigwart, *Experientia*, **19**, 488 (1963).

[9] B. J. Hathaway, D. G. Holah, and J. D. Postlethwaite, *J. Chem. Soc.*, **1961**, 321.

[10] J. Chatt and F. G. Mann, *ibid.*, **1940**, 1192.

[11] L. Horner, G. Mummenthey, H. Moser, and P. Beck, *Chem. Ber.*, **99**, 2782 (1966).

[12] Y. Hirusawa, M. Oku, and K. Yamamoto, This Bulletin, **30**, 667 (1957).

[13] G. V. Medoks and V. F. Andronova, *J. Gen. Chem. USSR*, **22**, 2113 (1952).

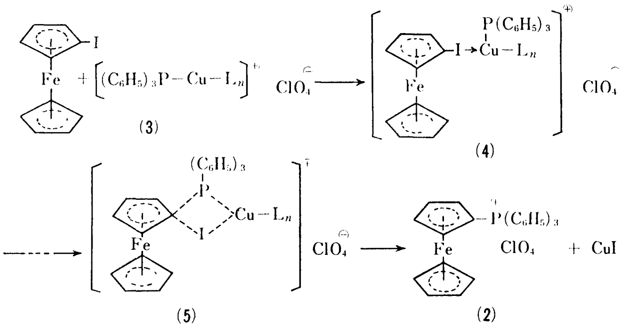
copper(I) perchlorate. Moreover, the solvent effect in this reaction was found to be astonishing. When acetonitrile or pyridine instead of nitromethane was used as the solvent in this reaction, no ferrocenyltriphenylphosphonium salt was obtained, but iodoferrocene was recovered almost quantitatively.

In order to get more information, the reaction was examined under various molar ratios of the three components, using nitromethane as the solvent. The results are summarized in Table 2.

As may be seen in the table, the yield of the phosphonium salt decreases drastically as the molar ratio of triphenylphosphine increases (Exp. 1—3). This fact, together with the solvent effect described above, suggests that the reaction is strongly affected by the ligands coordinated in the copper(I) complex which serves as the intermediate in the reaction. On the other hand, when 0.2 mol of tetrakis(acetonitrilo)copper(I) perchlorate was used against 1 mol each of iodoferrocene and triphenylphosphine, no reaction was observed and the starting material was recovered almost quantitatively (Exp. 4). This observation clearly indicates that the copper(I) complex does not act as a catalyst in this reaction, unlike as in a similar reaction in the benzene series.[10-13]

Discussion

When triphenylphosphine and tetrakis(acetonitrilo)-copper(I) perchlorate was dissolved in nitromethane, a homogeneous greenish-yellow solution was obtained. As the amount of triphenylphosphine in the solution increased, the color of the solution gradually changed from greenish-yellow to almost colorless. The change in color is probably due to the change in the ligands in the copper(I) complex. It is considered probable that, when tetrakis(acetonitrilo)copper(I) salt is dissolved in nitromethane, the acetonitrile molecule coordinated in the complex is replaced by the solvent molecule. An analogous complex, in which nitromethane coordinates to the copper(I) ion instead of acetonitrile, was reported recently.[14] When iodoferrocene was added to the nitromethane solution of tetrakis(acetonitrilo)copper(I) perchlorate containing triphenylphosphine, a homogeneous reddish-orange solution was obtained, and the reaction of iodoferrocene with triphenylphosphine took place when the solution was heated. A white precipitate, which is supposed to be copper(I) iodide, was separated out as the reaction proceeded, but no change in the color of the solution was observed during the reaction. If iodoferrocene is reduced by a copper(I) complex to produce the ferrocenyl radical and the copper(II) complex, the latter may react with iodoferrocene to give a ferricenium cation, and the color of the reaction mixture ought to change during the reaction. Accordingly, the above observation suggests that this reaction does not proceed through such a radical mechanism. It seems reasonable to assume that the first step in the formation of ferrocenyltriphenylphosphonium salt is the coordination of the iodine atom in iodoferrocene to the copper(I) ion of the complex **3**, coordinated with triphenylphosphine in advance. The unstable intermediate (**4**) thus formed would provide the final product (**2**) *via* a four-centered transition state (**5**), which might have a structure similar to that proposed for the halogen-exchange reaction of haloferrocene with copper(I) chloride.[5] This assumption is consistent with the results listed in Table 2. The coordination of iodoferrocene to the copper(I) ion is supposed to be weak, if it exists at all. Accordingly, if the amount of triphenylphosphine, which has a much stronger coordinating ability than iodoferrocene, increases, the copper(I) ion will be strongly coordinated by the triphenylphosphine; thus, the coordination by iodoferrocene will be obstructed, resulting in the reduction of the formation of ferrocenyltriphenylphosphonium salt. The solvent effect on this reaction also accords with the reaction mechanism proposed above; when acetonitrile or pyridine, which has a particular affinity to the copper(I) ion,[15] is used as a solvent, a similar obstruction of the coordination of iodoferrocene will retard the reaction.



L = CH_3CN and/or CH_3NO_2

Experimental

Materials. Iodoferrocene was prepared from chloromercuriferrocene by a slightly modified procedure of the previously-reported method.[16] Bromoferrocene was prepared from iodoferrocene according to the procedure described in a previous paper.[5] Tetrakis(acetonitrilo)copper(I) perchlorate was prepared according to the literature.[8] The solvents used in this study were purified by distillation.

Ullmann-type Coupling Reaction of Bromoferrocene Catalyzed by Tetrakis(acetonitrilo)copper(I) Perchlorate. To a pale yellow solution of tetrakis(acetonitrilo)copper(I) perchlorate (0.50 g, 0.0018 mol) in nitromethane[17] (20 m*l*), bromoferrocene (0.53 g, 0.0018 mol) was added at 44.5°C under a nitrogen atmosphere. The solution rapidly changed in color, from orange to black. After being heated at that temperature for 72 hr, the reaction mixture was poured into water containing tin(II) chloride. The mixture was extracted with benzene. The benzene solution was washed with water and dried over anhydrous magnesium sulfate. After the evaporation of the solvent under reduced pressure, the residue was chromatographed on alumina, using benzene - *n*-hexane (1 : 2) as the

---

[14] W. L. Driessen and W. L. Groeneveld, *Rec. Trav. Chim. Pays-Bas,* **88**, 491 (1969).

[15] I. M. Kolthoff and J. F. Coetzee, *J. Amer. Chem. Soc.*, **79**, 1852 (1957).

[16] H. Shechter and J. F. Helling, *J. Org. Chem.*, **26**, 1034 (1961).

[17] Nitromethane was bubbled with nitrogen before use in order to replace the dissolved oxygen with nitrogen.

solvent. From the first fraction of chromatographic separation, bromoferrocene (0.240 g, 45.3% recovery) was obtained, while from the second fraction, biferrocenyl (0.065 g, 35% yield) was isolated. The latter was recrystallized from benzene, mp 238°C (decomp.) (lit,[3] 239—240°C, decomp.), and identified by means of its NMR and IR spectra. Ferrocene could not be detected, even by gas-chromatographic analysis.

A similar reaction was attempted in acetonitrile instead of nitromethane, but it was unsuccessful.

The Reaction of Iodoferrocene with Triphenylphosphine in the Presence of Tetrakis(acetonitrilo)copper(I) Perchlorate in Nitromethane. Iodoferrocene (0.56 g, 0.0018 mol) was added, at 44.5°C in a nitrogen atmosphere, to a pale greenish-yellow solution of triphenylphosphine (0.47 g, 0.0018 mol) and tetrakis(acetonitrilo)copper(I) perchlorate (0.50 g, 0.0018 mol) in deoxygenated nitromethane[16] (20 m*l*). The color of the solution turned orange, but no further change in the color occurred during the reaction. After being heated at 101°C for 6 hr, the solution was filtered in order to remove the white precipitate separated during the reaction and the precipitate was washed with dichloromethane. The filtrate and the washing solution were then combined, and the combined solution was washed several times with water and then dried over anhydrous magnesium sulfate. The removal of the solvent under reduced pressure gave orange crystals. The crystals were dissolved again in dichloromethane, and then benzene was added to the solution. When dichloromethane was removed from the solution under reduced pressure, orange crystals of ferrocenyltriphenylphosphonium perchlorate (0.795 g, 80.8% yield) were separated out. The crystals were purified further by repeating the procedure described above; mp 175°C (decomp.). IR spectrum (KBr): 3100, 1414, 1008, 815 cm^{-1} (ferrocene nucleus); 1589, 1483, 749, 695 cm^{-1} (benzene ring); 1440, 994 cm^{-1} (P–C); and 1058—1113 cm^{-1} (perchlorate anion). NMR spectrum ($CDCl_3$): δ 4.15 (5H, singlet), 4.55 (2H, triplet), 4.90 (2H, triplet), 7.2—8.0 ppm (15H, multiplet).

Found: C, 60.83; H, 4.90%. Calcd for $C_{28}H_{24}O_4ClPFe$: C, 61.50; H, 4.43%.

Similar reactions were attempted in acetonitrile or pyridine instead of nitromethane, but they were in vain.