

REACTIONS OF CYCLOPENTADIENYL COPPER(I) TRIBUTYLPHOSPHINE WITH IODOBENZENES

ROBERT WAHREN

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm (Sweden)

(Received January 1st, 1973)

SUMMARY

Cyclopentadienylcopper(I) tributylphosphine reacts with iodobenzenes to give arylcyclopentadienes. If the iodobenzene has strongly electron-attracting substituents, copper-iodine exchange may occur simultaneously. The resulting transient arylcopper compounds have been trapped with acetyl chloride but may otherwise give symmetric biphenyls.

INTRODUCTION

Cyclopentadienylcopper(I) phosphine complexes, prepared from cyclopentadienylthallium¹ and from cyclopentadiene, a phosphine and copper(I) tert-butoxide² or copper(I) oxide³, have been characterised by X-ray crystallography^{4,5} and by NMR- and IR spectroscopy⁶. In the solid state, X-ray investigations show a π -bonded structure with a planar cyclopentadienyl ring. The room temperature NMR spectrum exhibits a single sharp peak for the protons of the cyclopentadienyl ring. At lower temperatures in some highly polar solvents this peak splits, indicating that less symmetric structures become increasingly important^{7,8}.

Several organocopper compounds are proving useful as reagents in organic synthesis^{9,10}. π -Bonded copper compounds with phosphine or isocyanide ligands, take part in interesting reactions. Cyclopentadienyl- and indenylcopper isocyanides catalyse reactions between cyclopentadiene and carbonyl compounds¹¹. Cyclopentadienylcopper tributylphosphine gives acyloxyfulvenes with acid chlorides¹². The briefly reported reaction between cyclopentadienylcopper tributylphosphine and iodobenzenes¹³ has now been studied more closely.

RESULTS

Cyclopentadienylcopper tributylphosphine reacts with iodobenzenes to give arylcyclopentadienes.

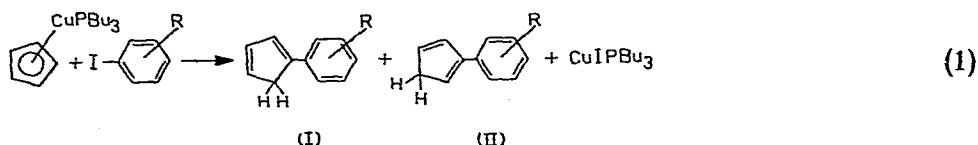


TABLE 1

YIELDS (% BASED ON THE IODOBENZENE) OF PRODUCTS FROM REACTIONS OF CYCLOPENTADIENYL COPPER TRIBUTYLPHOSPHINE AND AN EQUIMOLAR AMOUNT OF IODOARENE IN REFLUXING ETHER

R	(I), (II)	(III)	(IV)	Reaction time (h)
4-OCH ₃	75 ^a			50
4-CH ₃ ^b	50			50
H	75 ^a			50
4-COOCH ₃	60 ^a			50
2-COOCH ₃ ^b	34			24
2-COOH ^c	7	14	32	20
2-NO ₂ ^d	10	47	5	6
penta-F	4 ^a	8 ^a	60 ^{a,e}	9

^a Yields based upon GLC measurements. ^b *cf.* Ref. 13. ^c Room temperature; ether/dimethylformamide 1/1. ^d -30°. ^e After hydrolysis.

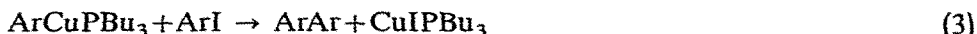
Strongly electron-attracting substituents on the iodoarene increase the reaction rates as well as the likelihood of side reactions such as dehalogenation and the formation of symmetric biaryls.

The rather unstable arylcyclopentadienes consist of approximately equal amounts of the 1- and 2-aryl-1,2,3,4,5-cyclopentadiene isomers [(I) and (II)]. However, they can be converted to the more stable 1,1'-diarylcyclopentadienes with iron(II) chloride or hydrogenated to arylcyclopentanes.

In some cases copper-iodine exchange competes with reaction 1.



The arylcopper formed can react further, for instance with an acid chloride to give a ketone¹⁴ or with an iodoarene to yield symmetric biaryls.



Acetophenones can be detected upon the addition of acetyl chloride to the reaction mixtures of cyclopentadienylcopper tributylphosphine and 2-iodonitrobenzene or pentafluoroiodobenzene, indicating that 2-nitrophenylcopper and pentafluorophenylcopper are intermediates formed by copper-iodine exchange reactions.

Copper-iodine exchange predominates in the reaction between cyclopentadienylcopper tributylphosphine and pentafluoroiodobenzene, pentafluorophenylcopper being accumulated in the solution. After nine hours a 60% conversion is reached (based on hydrolysis to pentafluorobenzene followed by GLC measurements). The concentration of pentafluorophenylcopper then decreases very slowly as coupling with pentafluoroiodobenzene occurs¹⁵. The pentafluorophenylcopper produced from cyclopentadienylcopper reacts with acetyl chloride, forming pentafluoroacetophenone.

The copper-iodine exchange (reaction 2) which produces an arylcopper compound, should also give iodocyclopentadiene. This is a very unstable compound which easily dimerises and forms a Diels-Alder adduct with *N*-phenyl-1,2,4-triazoline-3,5-dione¹⁶. Attempts to use this reagent to trap the iodocyclopentadiene formed in the copper-iodine exchange have not yet been successful. These experiments are complicated by the fact that cyclopentadienylcopper also reacts with *N*-phenyl-triazolidinedione.

The phosphine ligand on the copper atom has a marked effect on the reaction rates. Cyclopentadienylcopper triphenylphosphine or triethyl phosphite react much more slowly with methyl 2-iodobenzoate than does the tributylphosphine complex. Decreased rates of substitution with decreasing basicities of the phosphine ligands have been observed for several transition metal carbonyl complexes¹⁷.

The thermal stabilities of the copper complexes fall off in the order¹; $\text{CpCu-PPh}_3 > \text{CpCuPBu}_3 > \text{CpCu P(OEt)}_3$. The low thermal stability of the triethyl phosphite complex is probably the limiting factor in the reaction with methyl 2-iodobenzoate. After six hours in refluxing ether the solution has deposited some metallic copper and there is practically no reaction with the iodoarene.

No reaction has been observed between cyclopentadienylcopper tributylphosphine and "activated" bromoarenes (such as methyl 2-bromobenzoate) or iodoferrocene, even though the latter is as reactive as 2-iodonitrobenzene in Ullmann couplings¹⁸.

DISCUSSION

In the reaction between 2-iodonitrobenzene and cyclopentadienylcopper, 2-nitrophenylcopper is formed transiently as indicated by the detection of 2-nitroacetophenone when acetyl chloride is added at -30° . There is little accumulation of 2-nitrophenylcopper, although it may be stabilised to some extent by tributylphosphine. By way of comparison it should be noted that 2-nitrophenyllithium begins to decompose at -100° ¹⁹.

2-Nitrophenylcopper has been suggested as an intermediate in the decarboxylation of copper(I) 2-nitrobenzoate²⁰ and in the closely related "decarboxylative coupling" of 2-nitrobenzoic acid and iodobenzene with copper(I) oxide in quinoline to give 2-nitrobiphenyl^{21,22}. However, the reaction of cyclopentadienylcopper tributylphosphine with 2-iodonitrobenzene is the first instance where 2-nitrophenylcopper has been demonstrated to exist as a transiently formed intermediate.

Some dehalogenation occurs in the reactions of cyclopentadienylcopper and 2-iodonitrobenzene. The source of the protons replacing the iodine is not clear. Since acid is added during work up, it is conceivable that a protonation occurs at this stage. The dehalogenation may also be related to the "reductive dehalogenation" encountered in the Ullmann biaryl synthesis²³.

When the same reaction is run at room temperature, nitrobenzene is the only observed product. This may perhaps be related to the observation that in the reaction between 1,3-dinitrobenzene and 2-iodonitrobenzene with copper(I) oxide in quinoline, almost complete dehalogenation takes place to produce nitrobenzene^{24,25}.

Cyclopentadienylcopper tributylphosphine and 2-iodobenzoic acid form, in ether, a white sticky precipitate, the nature of which is not yet known. The addition of

dimethylformamide gives a homogeneous solution in which coupling and dehalogenation reactions take place. Phenylethynylcopper is known to react with 2-iodobenzoic acid to 2-(phenylethynyl)benzoic acid²⁶. In the copper-promoted Hurltley reaction, 2-bromobenzoic acid reacts with a variety of nucleophiles under mild conditions. From 2-bromobenzoic acid itself or its sodium salt and copper or copper(II) salts one can form benzoic acid, diphenic acid and salicylic acid²⁷.

The mechanisms of cyclopentadienylcopper reactions need further investigation. The rate of reaction is increased moderately by electron-attracting substituents on the iodoarene¹³ and also appears to rise with increasing basicity of the phosphine ligands. Judging from these observations, the reactions might be described in terms of oxidative additions²⁸.

Most arylcyclopentadienes are labile, becoming discoloured on exposure to air and tending to polymerise even at low temperatures. Phenylcyclopentadiene itself has been isolated only by chromatography on a column cooled to -20° . Electron attracting substituents on the phenyl ring seem to stabilize the system. (2-Nitrophenyl)cyclopentadiene can be stored at 4° for about one month without appreciable signs of dimerization.

All the arylcyclopentadienes isolated in this study are isomer mixtures, as shown by NMR. Thus, contrary to earlier reports²⁹, phenylcyclopentadiene itself consists of about equal amounts of two isomers [(I) and (II), R = H]. No 5-aryl-cyclopentadienes have been observed. Sublimation of a phenylcyclopentadiene isomer mixture results in material enriched in 1-phenylcyclopentadiene.

EXPERIMENTAL

Melting points were determined on a micro hot stage. NMR spectra were recorded on a Varian A 60 A spectrometer (TMS internal standard) and mass spectra on an LKB 9000 instrument. GLC was performed on a Varian Aerograph 204-1B with 5% SE 30 on Chromosorb W. Toluene or naphthalene was used as an internal standard. Reactions involving organometallic compounds were performed anhydrously under purified nitrogen. Diethyl ether was freshly distilled from lithium aluminium hydride. Cyclopentadienylcopper tributylphosphine was prepared from cyclopentadienylthallium as described earlier¹³. Copper(I) iodide triphenylphosphine³⁰ and copper(I) iodide triethylphosphite³¹ were prepared by methods reported in the literature. The structures of known compounds were checked by melting points, NMR, IR or mass spectroscopy.

General procedure for the coupling reactions

Cyclopentadienylcopper tributylphosphine dissolved in ether was added with a syringe to an equimolar amount of iodoarene in ether (50–100 ml). The solution was refluxed. In some cases small aliquots were withdrawn and analysed by gas chromatography. When the amount of iodoarene no longer decreased, silica gel was added, the ether evaporated and the organic components separated by column chromatography.

Cyclopentadienylcopper tributylphosphine and iodobenzene

Cyclopentadienylcopper (about 0.02 mol) and iodobenzene (0.02 mol) were

refluxed for 50 h. Separation of products and starting material was achieved on a column kept at -20° ³² eluting with mixtures of light petroleum (b.p. $40-45^{\circ}$) and benzene. The white crystals of phenylcyclopentadiene are highly unstable and quickly discolour in air. They begin to dimerise when kept under nitrogen at 4° overnight. Owing to this instability, the yield of isolated material was calculated on the basis of 1,1'-diphenylferrocene (see below). The NMR (CCl_4) showed two complex regions between τ 2.48 and 2.98 (relative area 5) and τ 3.17 and 3.78 (area 3) and two multiplets at τ 6.73 (area 1) and τ 6.89 ppm (area 1). Thus by analogy with previously studied compounds¹³, phenylcyclopentadiene consists of roughly equal amounts of 1-phenylcyclopentadiene [(I); $\text{R}=\text{H}$; τ 6.73 ppm] and 2-phenylcyclopentadiene [(II); $\text{R}=\text{H}$; τ 6.89 ppm]. The mass spectrum (70 eV) showed m/e 142 (100%) and 115 (38%).

1,1'-Diphenylferrocene

Phenylcyclopentadiene (from cyclopentadienylcopper tributylphosphine 0.02 mol and iodobenzene 0.02 mol) was reacted with butyllithium (0.025 mol) in tetrahydrofuran for 1 h. This solution was added with a syringe to a freshly prepared suspension of iron(II) chloride (0.025 mol) in tetrahydrofuran, and the mixture was stirred overnight. It was then poured into ice water, the ferrocene was extracted with ether and run through a column of silica gel to remove traces of iron chlorides. Recrystallisation from petroleum ether (b.p. $40-45^{\circ}$) gave 1,1'-diphenylferrocene 1.1 g, 32% (based on iodobenzene) m.p. $157-158^{\circ}$ (lit.³³ 154°). NMR showed the phenyl protons as a multiplet between τ 2.55 and 3.05 ppm (relative area 10) and the ferrocene protons as multiplets at τ 5.67 (area 4) and τ 5.92 ppm (area 4). The mass spectrum (20 eV) showed m/e 338 (100%), 197 (5%) and 141 (2%).

Cyclopentadienylcopper tributylphosphine and 2-iodonitrobenzene

Cyclopentadienylcopper (about 0.01 mol) and 2-iodonitrobenzene (0.01 mol) were stirred in ether at -30° for 6 h. Column chromatography with carbon tetrachloride/chloroform mixtures gave 2,2'-dinitrobiphenyl (0.57 g; 47%), (2-nitrophenyl)cyclopentadiene (0.18 g; 10%), 2-iodonitrobenzene (0.38 g; 15%) and nitrobenzene (0.06 g; 5%). The NMR spectrum of (2-nitrophenyl)cyclopentadiene, obtained as a yellow oil, showed two complex regions between τ 2.22-2.85 (relative area 4) and τ 3.25-3.55 (area 3) and two multiplets at τ 6.72 (area 1) and τ 6.82 ppm (area 1). Thus (2-nitrophenyl)cyclopentadiene likewise consists of about equal amounts of two isomers, 1-(2-nitrophenyl)cyclopentadiene [(I); $\text{R}=2\text{-NO}_2$; τ 6.72 ppm] and 2-(2-nitrophenyl)cyclopentadiene [(II); $\text{R}=2\text{-NO}_2$; τ 6.82 ppm]. The mass spectrum (70 eV) gave m/e 187 (44%), 139 (41%), 130 (100%) and 115 (85%).

(2-Nitrophenyl)cyclopentadiene (100 mg) was hydrogenated with palladium on charcoal in ethanol and the product was treated with acetic anhydride to give 2-cyclopentylacetanilide, 32 mg (30%), m.p. $111-112^{\circ}$. The mass spectrum (20 eV) gave m/e 203 (70%), 188 (32%) and 160 (100%). (Found: C, 76.6; H, 8.4; N, 6.8. $\text{C}_{13}\text{H}_{17}\text{NO}$ calcd.: C, 76.8; H, 8.4; N, 6.9%.)

In another experiment cyclopentadienylcopper (about 0.01 mol) and 2-iodonitrobenzene (0.01 mol) was stirred in ether at -30° for 0.5 h, after which acetyl chloride (0.1 mol) was added. The mixture was stirred for a further half hour, then hydrolysed with an aqueous ammonia/ammonium chloride solution, and the ether

phase was washed with water, dried and examined by gas chromatography-mass spectrometry. Small amounts (about 1% based on 2-iodonitrobenzene) of a substance were detected which showed the following mass spectrum (20 eV) m/e 165 (4%), 150 (100%), 123 (13%) and 92 (8%). An authentic sample of 2-nitroacetophenone gave an identical spectrum. Identical spectra were also obtained at 70 eV.

Cyclopentadienylcopper tributylphosphine and pentafluoriodobenzene

Cyclopentadienylcopper tributylphosphine (about 0.01 mol) and pentafluoriodobenzene (0.01 mol) were boiled under reflux. Samples were withdrawn at intervals, hydrolysed and analysed by gas chromatography. After 9 h the amount of (pentafluorophenyl)cyclopentadiene (4%) no longer increased. The solution contained about 8% of decafluorobiphenyl and 60% of pentafluorobenzene. The amount of pentafluorobenzene then decreased very slowly (over 50% remained after 25 h) and the amount of biphenyl slowly increased. Samples not subjected to hydrolysis showed no pentafluorobenzene. The mass spectrum of (pentafluorophenyl)-cyclopentadiene showed m/e 232 (100%) and 213 (30%).

In another experiment, cyclopentadienylcopper tributylphosphine (about 0.01 mol) and pentafluoriodobenzene (0.01 mol) were refluxed together for 20 h. Acetyl chloride (0.1 mol) was then added and the mixture was stirred for another 10 h. After hydrolysis with aqueous ammonia/ammonium chloride the organic components were separated by column chromatography (silica gel, CCl_4) giving pentafluoroacetophenone (0.496 g; 24%), $n_D^{17.5}$ 1.4340 (lit.³⁴ $n_D^{17.5}$ 1.4335) and decafluorobiphenyl, 0.424 g (26%).

Cyclopentadienylcopper tributylphosphine and 2-iodobenzoic acid

To a stirred solution of cyclopentadienylcopper (about 0.01 mol) in ether/dimethylformamide, 2-iodobenzoic acid (0.01 mol) was added at -30° . The solution slowly warmed to room temperature and was stirred for 20 h before being hydrolysed with aqueous ammonia/ammonium chloride and acidified with hydrochloric acid. The organic acids were extracted with potassium carbonate and converted into methyl esters with diazomethane. These were then separated by column chromatography (silica gel, benzene) giving methyl benzoate (0.423 g; 32%), methyl 2-(cyclopentadienyl)benzoate¹³ (0.130 g; 7%) and dimethyl diphenate (0.190 g; 14%). When ether alone was used as the solvent, a white sticky material separated already at -30° . This did not react further. The addition of dimethylformamide rendered the solution homogenous again. GLC revealed no non-acid reaction products.

Cyclopentadienylcopper tributylphosphine and 4-methoxyiodobenzene

Cyclopentadienylcopper tributylphosphine (about 0.01 mol) and 4-methoxyiodobenzene (0.01 mol) were refluxed. Samples were withdrawn and analysed by gas chromatography-mass spectrometry. GLC indicated about 75% of 4-(cyclopentadienyl)anisole after 50 h. No biphenyl was detected. The mass spectrum (70 eV) on the cyclopentadienylanisole gave m/e 172 (100%), 157 (61%) and 128 (57%).

Cyclopentadienylcopper tributylphosphine and methyl 4-iodobenzoate

Cyclopentadienylcopper (about 0.01 mol) and methyl 4-iodobenzoate (0.01 mol) were refluxed. Samples were withdrawn and analysed by gas chromatography-

mass spectroscopy. GLC indicated about 60% of methyl 4-(cyclopentadienyl)benzoate after 50 h. No biphenyl was detected. The mass spectrum (70 eV) of methyl 4-(cyclopentadienyl)benzoate gave $m/e=200$ (96%), 169 (100%), 141 (38%) and 115 (48%).

Cyclopentadienylcopper triphenylphosphine and methyl 2-iodobenzoate

Cyclopentadienylcopper triphenylphosphine (about 0.01 mol; prepared according to ref. 1) and methyl 2-iodobenzoate (0.01 mol) were stirred in tetrahydrofuran at 40°. Samples were withdrawn and analysed by gas chromatography-mass spectrometry. After 50 h about 10% methyl 2-(cyclopentadienyl)benzoate had been formed.

Cyclopentadienylcopper triethyl phosphite and methyl 2-iodobenzoate

Cyclopentadienylcopper triethyl phosphite (about 0.01 mol; prepared according to ref. 13) and methyl 2-iodobenzoate (0.01 mol) were refluxed in ether. Samples were withdrawn and analysed by gas chromatography-mass spectrometry. After 6 h about 30% of methyl 2-(cyclopentadienyl)benzoate had been formed. Very little additional product was obtained when the reaction time was prolonged.

ACKNOWLEDGEMENTS

This work has been supported by the Swedish Board for Technical Development. I thank Professor Martin Nilsson and Dr. Olof Wennerström for their interest and valuable discussions. Mr. Ronny Lundin has given skillful technical assistance. The NMR spectra were recorded by Mr. Egon Pettersson. The English was checked by Patrick Hort. I also thank ISC Chemicals Ltd. for a sample of pentafluoriodobenzene.

REFERENCES

- 1 F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **92** (1970) 5114.
- 2 T. Tsuda, T. Hashimoto and T. Saegusa, *J. Amer. Chem. Soc.*, **94** (1972) 658.
- 3 G. Wilkinson and T. S. Piper, *J. Inorg. Nucl. Chem.*, **2** (1956) 32.
- 4 F. A. Cotton and J. Takats, *J. Amer. Chem. Soc.*, **92** (1970) 2353.
- 5 L. T. J. Delbaere, D. W. McBride and R. B. Ferguson, *Acta Crystallogr. Sect. B*, **26** (1970) 515.
- 6 F. A. Cotton and T. J. Marks, *J. Amer. Chem. Soc.*, **91** (1969) 7281.
- 7 G. M. Whitesides and J. S. Fleming, *J. Amer. Chem. Soc.*, **89** (1967) 2855.
- 8 C. H. Campbell and M. L. H. Green, *J. Chem. Soc. A*, (1970) 1318.
- 9 J. F. Normant, *Synthesis*, (1972) 63.
- 10 G. H. Posner, *Organic Reactions*, **19** (1972) 1.
- 11 T. Saegusa, Y. Ito and S. Tomita, *J. Amer. Chem. Soc.*, **93** (1971) 5656.
- 12 R. Lundin, C. Moberg, R. Wahren and O. Wennerström, *Acta Chem. Scand.*, **26** (1972) 2045.
- 13 M. Nilsson, R. Wahren and O. Wennerström, *Tetrahedron Lett.*, (1970) 4583.
- 14 H. Gilman and J. M. Straley, *Recl. Trav. Chim. Pays-Bas*, **55** (1936) 821.
- 15 R. DePasquale and C. Tamborski, *J. Org. Chem.*, **34** (1969) 1736.
- 16 R. Breslow and J. M. Hoffman, *J. Amer. Chem. Soc.*, **94** (1972) 2110.
- 17 R. J. Angelici, *Organometal. Chem. Rev., Sect. A*, **3** (1968) 173.
- 18 M. D. Rausch, *J. Org. Chem.*, **26** (1961) 1802.
- 19 P. Buck, *Angew. Chem.*, **81** (1969) 136.
- 20 J. Chodowska-Palicka and M. Nilsson, *Acta Chem. Scand.*, **24** (1970) 3353.

- 21 M. Nilsson, *Acta Chem. Scand.*, 20 (1966) 423.
- 22 A. Cairncross, J. R. Roland, R. M. Henderson and W. A. Sheppard, *J. Amer. Chem. Soc.*, 92 (1970) 3187.
- 23 R. G. R. Bacon and H. A. O. Hill, *Quart. Rev.*, 19 (1965) 95.
- 24 C. Björklund and M. Nilsson, *Acta Chem. Scand.*, 22 (1968) 2338.
- 25 C. Björklund, *Copper Promoted Arylation of Nitroarenes*, diss. Stockholm, 1972.
- 26 C. E. Castro, R. Havlin, V. K. Honwad, A. Malte and S. Mojé, *J. Amer. Chem. Soc.*, 91 (1969) 6464.
- 27 W. R. H. Hurlley, *J. Chem. Soc.*, (1929) 1870.
- 28 J. P. Collman, *Accounts Chem. Res.*, 1 (1968) 136.
- 29 R. Riemschneider and R. Nerin, *Monatsh. Chem.*, 91 (1960) 829.
- 30 G. B. Kauffman and L. A. Teter, *Inorg. Syn.*, 7 (1963) 9.
- 31 A. Arbusoff, *Chem. Ber.*, 38 (1865) 1171.
- 32 N. G. Johansson, *Acta Chem. Scand.*, to be published.
- 33 P. L. Pauson, *J. Amer. Chem. Soc.*, 76 (1954) 2187.
- 34 A. E. Jukes, S. S. Dua and H. Gilman, *J. Organometal. Chem.*, 21 (1970) 241.