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REACTION OF TRIBUTYLPHOSPHINE (PENTAHAPTOCYCLOPENTADIENYL) COPPER (I) WITH IODOARENES

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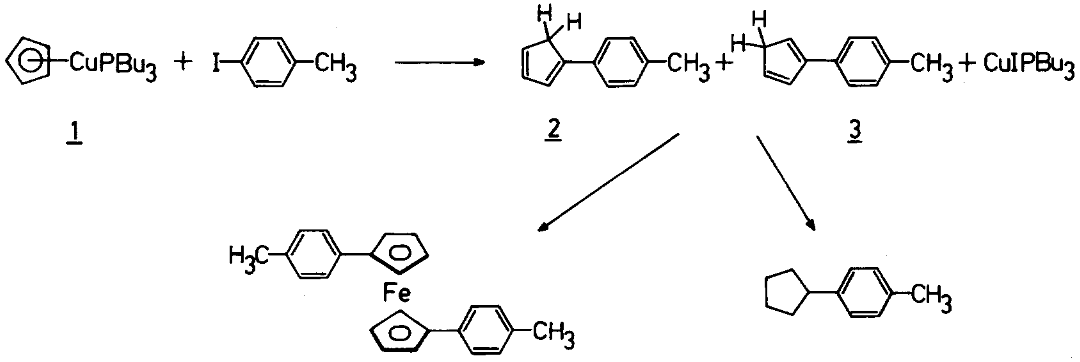
Cyclopentadienylcopper complexes with triphenyl- and triethylphosphine have been shown recently to be of the pentahapto type.[1,2] The present investigation was undertaken to see whether a π-bonded copper complex would react with iodoarenes in a way similar to σ-bonded copper compounds like alkyl-,[3] alkenyl-,[4] alkynyl-,[5] phenyl-,[6] and 2-thienyl copper.[7] If so, this would be in analogy with π-allyl nickel complexes, which react with halogenoarenes to give unsymmetrical coupling products.[8]

Cyclopentadienylcopper tributylphosphine (1) was prepared from cyclopentadienylthallium as suggested by Cotton.[9] An etheral solution of $(CuIP(C_4H_9)_3)_4$ (2.5 mmole) was slowly added to a suspension of cyclopentadienylthallium (10 mmole) in ether at 0° [x]. Orange thallium (I) iodide



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[x] Reactions involving organometallic compounds were performed anhydrously under purified nitrogen.

precipitated (99 %). Stirring was continued for 10 minutes after the addition had been completed. Cyclopentadienylcopper tributylphosphine is soluble in ether. The colourless homogenous solution was withdrawn with a syringe for further reactions.

Cyclopentadienylcopper (approx. 10 mmole) was reacted with 4-iodotoluene (10 mmole) in refluxing ether for 50 h. The reaction mixture was separated on a silica gel column to give 4-cyclopentadienyltoluene (50 %) and unreacted iodide (22 %).

The NMR spectrum (solvent CCl_4) showed a complex region between τ=2.45 and 3.10 (relative area 4) and multiplets at τ=6.70 (area 1) and τ=6.86 (area 1). In view of the fact that the methylenic protons in cyclopentadiene have a τ value of 7.00, the NMR data were interpreted on the assumption that the coupling product consisted of approximately equal amounts of 4-(2,4-cyclopentadien-2-yl) toluene (2, τ=6.70) and 4-(2,4-cyclopentadien-3-yl) toluene (3, τ=6.86).

Cyclopentadienylalkanes are known to rearrange under mild conditions to mixtures of 2- and 3-cyclopentadienyl isomers.[10] The isolated coupling product was a strongly fluorescent oil-crystal mixture. After sublimation it gave a crystalline mixture, m.p. 72 - 78°, roughly consistent with a 4 to 1 ratio of compounds 2 and 3, as seen by NMR spectroscopy.

The mass spectrum (70 eV) showed the molecular ion at m/e = 156 (100 %).

Methyl 2-iodobenzoate reacted with 1 for 24 h in refluxing ether to give methyl 2-(cyclopentadienyl) benzoate in 34 % yield (13 % unreacted iodide). The yield of coupling products was unchanged when the thallium (I) iodide from the first reaction was not removed. Cyclopentadienylthallium does not react with methyl 2-iodobenzoate in refluxing ether.

The NMR spectrum (solvent $CDCl_3$) showed multiplets at τ=6.70 (relative area 1) and 6.86 (area 1) and two peaks at τ=6.22 (combined area 3) 0.7 Hz apart (measured with a 100 MHz instrument). In this case, too, the isolated product, a yellow fluorescent liquid, consisted of nearly equal amounts of the 2- and 3-cyclopentadienyl isomers. These could be separated on GLC and had almost identical mass spectra.

The mass spectrum (70 eV) showed the molecular ion at m/e = 200 (22 %) and the base peak at m/e = 168 (M-32).

Both phenylcyclopentadienes were easily hydrogenated with palladium on charcoal to the corresponding phenylcyclopentanes.

4-(Cyclopentyl) toluene gave an NMR spectrum (solvent CCl_4) with a single aromatic peak, no ethylenic protons, and a broad methylene peak around τ=8.3.

The mass spectrum (70 eV) showed the molecular ion at m/e = 160 (58 %) and the base peak at m/e = 131 (M-29).

Methyl 2-(cyclopentyl) benzoate gave an NMR spectrum (CCl_4) with a single methyl ester peak at τ=6.22, no ethylenic protons, and a broad methylene peak around τ=8.3. The mass spectrum (70 eV) showed the molecular ion at m/e = 204 (32 %) and the base peak at m/e = 144 (M-60).

1,1-Ditolylferrocene was obtained from the tolylcyclopentadiene, using butyllithium and iron (II) chloride (yield 21 %, m.p. 175-179°).

The NMR spectrum (solvent CCl_4) showed the ferrocene protons as multiplets at τ=5.59 and 5.84. The mass spectrum (20 eV) gave the molecular ion at m/e = 366 (100 %). The second largest peak was at m/e = 156 (3 %), equivalent to ionised tolylcyclopentadiene. The infrared spectrum (KBr) was in accordance with that given by Nesmeyanov.[11]

When kept at 4° 4-(cyclopentadienyl) toluene dimerises in about a week, methyl 2-(cyclopentadienyl) benzoate in about a month. At room temperature both compounds polymerise irreversibly in a few days.

In π-cyclopentadienylcopper phosphines, the copper atom has 18 electrons in the outer shell and thus is not prone to coordinate further. σ-Bonded organocopper compounds like ethynyl- and phenylcopper can coordinate with other groups.[5,6] The ortho-effect reported for copper-promoted reactions has been attributed to such coordinations. In this investigation the increase observed in the reaction rate was only moderate, going from 4-iodotoluene to methyl 2-iodobenzoate. A drastic example of the ortho-effect is provided when copper (I) phenylacetylide reacts with iodobenzene and 2-iodobenzoic acid, the rate constants being 8.0×10^{-6} and 7.0×10^{-2} $l\ mole^{-1} sec^{-1}$ respectively.[5]

Metal-halogen exchange has been reported for alkyl- and arylcopper reactions with halogenoarenes.[3,6] In the present case no biphenyls were observed, indicating that metal-halogen exchange is of less importance.

Phenylcyclopentadienes are of interest in connection with organic dye lasers[12] and the preparation of substituted ferrocenes.[13]

The literature concerning cyclopentadienylarenes is scarce. Phenylcyclopentadiene has been prepared from bromoacetophenone and ethyl acetoacetate.[14] Synthesis via cyclopentadienylcopper may prove to be a general route to these rather inaccessible and little studied compounds.

Acknowledgements

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References

1. F.A. Cotton and J. Takats, J.Am.Chem.Soc., 92, 2353 (1970).
2. L.T.J. Delbaere, D.W. McBride and R.B. Ferguson, Acta Cryst.Sekt.B, 26, 515 (1970).
3. E.J. Corey and G.H. Posner, J.Am.Chem.Soc., 90, 5615 (1968).
4. M. Nilsson and R. Wahren, J.Organometal.Chem., 16, 515 (1969)
5. C.E. Castro, R. Havlin, V.K. Honwad, A. Malte and S. Mojé, J.Am.Chem.Soc., 91, 6464 (1969).
6. M. Nilsson and O. Wennerström, Acta Chem.Scand., 24, 482 (1970).
7. M. Nilsson and C. Ullenius, Acta Chem.Scand., In press.
8. E.J. Corey and M.F. Semmelhack, J.Am.Chem.Soc., 89, 2755 (1967).
9. F.A. Cotton and T.J. Marks, J.Am.Chem.Soc., 91, 7281 (1969).
10. V.A. Mironov, E.V. Sobolev and A.N. Elizarova, Tetrahedron, 19, 1939 (1963).
11. A.N. Nesmeyanov, L.A. Kazitsyna, B.V. Lokshin and V.D. Vilchevskaia, Doklady Akad. Nauk S.S.S.R., 125, 1037 (1959).
12. P.M. Rentzepis and M.A. Duguay, Appl. Phys.Letters, 11, 218 (1967).
13. D.E. Bublitz and K.L. Rinehart, Org. React., 17, 37 (1969).
14. R. Riemschneider and R. Nerin, Monatsh.Chem., 91, 829 (1960).