

(Trichloromethyl)cyclopentadiene
from π -Cyclopentadienyl-
[(trichloromethyl)cyclo-
pentadiene]cobalt

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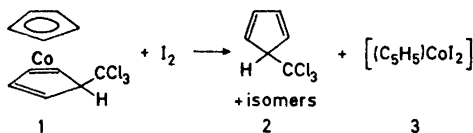
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We have previously found that nickelocene reacts with tetrachloromethane in the presence of triphenylphosphine to give, besides π -cyclopentadienyl(triphenylphosphine)nickel chloride,¹ (trichloromethyl)cyclopentadiene, which can be dehydrohalogenated to 6,6-dichlorofulvene.²

Cobaltocene is known to react with tetrachloromethane to give π -cyclopentadienyl[(trichloromethyl)cyclopentadiene]cobalt (1) and cobalticinium chloride.³ We have now found that (trichloromethyl)cyclopentadiene also can be formed from the complex (1).

It has been reported that ligands having acceptor properties, e.g. tetracyanoethylene sulphur dioxide, iodine, Ag(I),⁴ and trifluorophosphine⁵ displace ethylene from π -cyclopentadienyldiethylenerrhodium. The rhodium complex is inert to nucleophilic ligands, e.g. triphenylphosphine and carbon monoxide.³

The cobalt complex (1), which has an electron configuration analogous to that of the rhodium complex, shows a similar reactivity. On reaction with one mol of iodine it gives, after distillation, a 62% yield of (trichloromethyl)cyclopentadiene (after 1 h at 0° in diethyl ether, nitrogen atmosphere). The product is identical to (trichloromethyl)cyclopentadiene obtained earlier (GLC, MS NMR). A cobalt complex which probably has the composition (3) precipitates from the reaction mixture. Purification of this complex was unsuccessful.



Silver nitrate and tetracyanoethylene react with complex (1) to (trichloromethyl)cyclopentadiene in yields of 49% (after 16 h at 20°) and 50% (after 1 h at 0°), respectively. In the latter case ca. 5% of a Diels Alder adduct from (trichloromethyl)cyclopentadiene and tetracyanoethylene, apparently 2,2,3,3-tetracyano-7-(trichloromethyl)bicyclo[2.2.1]hept-5-ene, is also formed. (Found: C 46.2; H 1.6; N 17.9. Calc. for C₁₂H₅N₄Cl₃: C 46.3; H 1.6; N 18.0). Its NMR spectrum in DMSO-*d*₆ shows multiplets centered at $\delta = 3.50$ (1H), 4.68 (2H) and 6.65 (2H, triplet) and its mass spectrum shows the highest *m/e* values at 274/276/278 (M⁺ - HCl). Sulphur dioxide reacts more slowly with the complex (1). The yield of (trichloromethyl)cyclopentadiene after 24 h at 20° is merely 5%.

(Trichloromethyl)cyclopentadiene is displaced slowly and in a poor yield by tributylphosphine or triphenylphosphine (the estimated yield after several days is less than 8%, GLC). Surprisingly a few per cent of chlorobenzene is formed in these reactions (MS evidence).

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