# Reaction of Metal Atoms with Solutions; Preparation of Bis(cyclo-octa-1,5-diene)iron(0)

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*Summary* A technique has been developed for reacting metal atoms with solutions of compounds in inert solvents at temperatures up to 0°; it has been applied to the preparation of bis(cyclo-octa-1,5-diene)iron(0), a useful new starting material in iron chemistry.

THE work of Skell[1] on the vaporisation of carbon under vacuum and condensation of the vapour species with vapours of organic compounds on a liquid nitrogen cooled surface, established a technique which has been used in most subsequent studies of atom reactions.

We are now using a different method in which metal atoms are condensed into a solution of a reactant (2—20% w/v) in an inert solvent. The solution (50—200 ml) is contained in a continuously evacuated 2 l flask rotating at 50—80 r.p.m. Metal is vaporized upwards from a resistively heated crucible into the film of solution carried over on the top inside surface of the flask (see Figure). The design of the rotating flask system owes much to Green.[2]

The flask rotates in a cooling bath maintained at a temperature at which the vapour pressure of the solution is less than $10^{-3}$ Torr, so that the vacuum in the flask permits efficient vaporisation of the metal. Provided that the solvent and solute have low vapour pressures, it is possible to condense metal atoms into a solution at near room temperature. For example, nickel vapour condensed into a 10% solution of triphenylphosphine in Silicone 704 at 0° gave an excellent yield of $Ni(PPh_3)_4$. However, lower temperatures are used more commonly to reduce the vapour pressure of the solutions and to stabilise the products of reactions. Compounds which are too involatile or too unstable to be volatilised can be reacted with metal atoms provided that they are soluble in an inert solvent. Except when using very involatile solvents, the method gives products in a convenient form for isolation by standard solution techniques or for further reaction with other compounds added to the rotary reactor. We believe the yields of products to be higher in the solution method than by condensation at −196°.

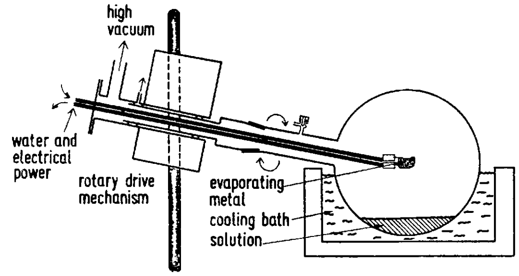

Figure. Apparatus for treating solutions of compounds with metal atoms

The main difficulty with the method is the choice of solvent. The Table shows the temperature at which some fairly inert liquids have a suitably low vapour pressure while retaining their mobility and their solvent character.

We have applied the method to reaction of iron vapour with 1,5-cyclo-octadiene, hoping to make an analogue of the well known bis(cyclo-octa-1,5-diene)nickel(0).

Two grams of iron vapour were condensed in an hour into 200 ml of a 10% solution of cyclo-octa-1,5-diene in methylcyclohexane at −120° in the rotary apparatus. The products were then washed out of the flask with cold pentane and the solution yielded several grams of a brown crystalline solid. The crystals or their green solution in pentane rapidly decomposed to metallic iron above −20°, but a solution in cyclo-octa-1,5-diene was slightly more stable. The compound did not react with dry nitrogen but caught fire in air.

The compound was decomposed quantitatively on treatment with a solution of 2,2′-bipyridyl in diethyl ether at −30°, followed by air oxidation and addition of $NH_4PF_6$. The products were two mols of cyclo-octa-1,5-diene and one mol of $Fe(bipy)_3(PF_6)_2$ indicating the formula $(C_8H_{12})_2Fe$ (an independent analysis gave Fe 20·3%, calc. 20·5%). The i.r. spectrum of the compound in a Nujol mull at −30° closely resembled that of bis(cyclo-octa-1,5-diene)nickel(0). When the compound was treated with trifluorophosphine at −30° in n-hexane, (cyclo-octa-1,5-diene)$Fe(PF_3)_3$ was formed. Cyclo-octatetraene reacted with the compound at −30° to form $(COT)_2Fe$; cyclo-octa-1,5-diene was liberated almost quantitatively.

Table

Solvents for metal atom reactions

| Solvent | Operating temperature/°C |
|---|---|
| Propane | −180 to −185 |
| Isopentane | −145 to −160 |
| Methylcyclohexane | −110 to −125 |
| *m*-Di-isopropylbenzene[a] | − 60 to −100 |
| Bis(ethylhexyl) ether[a] | − 10 to −60 |
| Light liquid paraffin | + 20 to 0 |
| Silicone 704[a] (a phenylmethylsiloxane) | + 50 to −20 |

[a] Some transition metal atoms react with these solvents.

The results suggest that we have made bis(cyclo-octa-1,5-diene)iron(0). Two structures of this compound seem possible, involving a square planar or a tetrahedral arrangement of the four olefinic bonds about the iron. The tetrahedral structure should be paramagnetic for a $d^8$ metal and the square planar structure diamagnetic. Solutions of the compound have given no $^1H$ n.m.r. signal possibly indicating that the compound is paramagnetic, but n.m.r., e.s.r., and magnetic balance measurements have all been rendered uncertain by the ready decomposition of the compound to metallic iron. A low-temperature *X*-ray crystal structure determination is to be attempted.

The compound is proving a very useful starting material in iron(0) chemistry. It can frequently be used without purification simply by adding other ligands to the slurry of the crude product in the rotary reactor.

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[1] P. S. Skell and L. D. Westcott, *J. Amer. Chem. Soc.*, 1963, **85**, 1023.

[2] F. W. S. Benfield, M. L. H. Green, J. S. Ogden, and D. Young, *J.C.S. Chem. Comm.*, 1973, 866.