Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

A NOVEL CYCLOOCTATETRAENE COMPLEX OF MOLYBDENUM

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(Received November 14th, 1969; in revised form December 9th, 1969)

SUMMARY

Reaction of cyclooctatetraene with molybdenum tetrachloride oxide gives a novel type of compound, of formula $MoOCl_2(C_8H_7)_2$, in which cyclooctatetraene is present in the form of cyclooctatetraenyl anion.

INTRODUCTION

Cyclooctatetraene has been reported to form addition complexes (π-type) and extensive study has been carried out with Group VIII elements[1-3]. The only complex of molybdenum isolated from the reaction of $Mo(CO)_6$ with cyclooctatetraene is $(C_8H_8)_2Mo(CO)_4$, which seems to contain a dimer of cyclooctatetraene[4,5].

There is no reference in the literature to substitution reactions of cyclooctatetraene with metal halides and metal halide oxides. Recently we have performed[6,7] substitution reactions of cycloheptatriene and chlorides and chloride oxides of the metals of Groups IV, V and VI. From the reaction of cyclooctatetraene with molybdenum tetrachloride oxide we have now isolated a compound having formula $MoOCl_2(C_8H_7)_2$, in which the cyclooctatetraene exhibits novel behaviour in acting as a cyclooctatetraenyl anion. Similar experiments with other halides and halide oxides of the metals of Groups IV, V and VI are in progress.

EXPERIMENTAL

Special precautions were taken to exclude moisture. Molybdenum tetrachloride oxide, $MoOCl_4$ was prepared by the method reported by Colten *et al.*[8]. Benzene dried with and distilled from sodium was further purified by azeotropic distillation with ethyl alcohol. The IR spectrum (in potassium bromide) was recorded on a Perkin–Elmer Model 137 spectrophotometer.

Preparation of dicyclooctatetraenylmolybdenum dichloride oxide

To 1.85 g of molybdenum tetrachloride oxide in 75 ml of dry benzene, added 1.55 g of cyclooctatetraene. The contents were refluxed till there was no further evolution of hydrogen chloride. The greenish blue compound thus obtained was dried under reduced pressure. (Found: C, 49.25; Cl, 18.20; Mo, 24.52. $C_{16}H_{14}Cl_2MoO$ calcd.: C, 49.36; Cl, 18.25; Mo, 24.66%.)

RESULTS AND DISCUSSION

Cyclooctatetraene can form a bond with a transition metal in the following ways:

(*i*). According to Raphael[9], in the tub conformation cyclooctatetraene coordinates via the 1,5-double bonds, like 1,5-cyclooctadiene, two double bonds not being involved. It could also act as a bridging group, the 1,5- and 3,7-double bonds being coordinated to two metal atoms.

(*ii*). In the conformation other than the tub, cyclooctatetraene forms mononuclear diene complexes in which one planar diene unit is attached to a metal atom or it could behave as a bridging group with two diene units each attached to two metal atoms.

It has been reported[10,11] that cyclooctatetraene can be reduced by alkali metals or at a dropping mercury electrode to give the planar cyclooctatetraenyl dianion, which has ten π-electrons and should behave according to Hückel's rule as an aromatic system. From the spectroscopic studies Lippincott and coworkers[12] have concluded that the vibrational spectra of cyclooctatetraene can be interpreted either on the basis of D_4 structure (crown structure) or on the basis of D_2d structure (tub conformation), with the evidence strongly in favour of D_4 structure.

Two moles of cyclooctatetraene react with one mole of molybdenum tetrachloride oxide with the evolution of two moles of hydrogen chloride, and the reaction may be represented as:

$$MoOCl_4 + 2\,C_8H_8 \rightarrow MoOCl_2(C_8H_7)_2 + 2\,HCl$$

The evolution of hydrogen chloride began as soon as refluxing was started and continued for 48 h. The nature of the product was unchanged when an excess of cyclooctatetraene was used.

Interpretation of the IR spectrum

Details of the spectrum are given in Table 1. The strong band at 980 cm^{-1} can be attributed to M=O stretching. The C–H stretching vibration appears as a band of medium intensity at 3000 cm^{-1}. The C=C stretching vibration can be associated with the medium band at 1635 cm^{-1}. The strong band at 752 cm^{-1} is probably associated with C–H bending while the bands at 695 cm^{-1}, 1400 cm^{-1} and 1450 cm^{-1} may be due to ring distortion. The band at 900 cm^{-1} can be assigned to the C–C stretching frequency.

TABLE 1

IR SPECTRUM OF DICYCLOOCTATETRAENYLMOLYBDENUM DICHLORIDE OXIDE (CM^{-1})

695 s, 752 s, 900 vw, 980 vs, 1400 m, 1450 m, 1485 w,
1540 vw, 1560 vw, 1635 m, 2385 s, 3000 m, 3300 w, 3500 w

ACKNOWLEDGEMENTS

We thank the Council of Scientific and Industrial Research, New Delhi, India, for the award of a Research Fellowship to K.M.S.

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