Journal of Organometallic Chemistry, 171 (1979) 365—367

PHOTOINDUCED REACTION OF PERCHLOROCYCLOPENTADIENE WITH $Mn_2(CO)_{10}$

MIHIR KANTI CHAUDHURI

Department of Chemistry, North Eastern Hill University, Shillong 793 003 (India)

(Received October 9th, 1978)

Summary

Perchlorocyclopentadiene, C_5Cl_6, and $Mn_2(CO)_{10}$ produce $C_5Cl_5^{\cdot}$, $Cl^{\cdot}$ and $(CO)_5Mn^{\cdot}$ radicals upon UV-irradiation, and these then react among themselves to give ultimately $Mn(\eta^1\text{-}C_5Cl_5)(CO)_5$, $Mn(CO)_5Cl$, and $C_{10}Cl_{10}$. The products were characterised by elemental analysis, IR and mass spectral studies. The mass spectrum of pentacarbonyl(η^1-pentachlorocyclopentadienyl)manganese is discussed.

Introduction

The synthesis, reactions and structural features of perchlorocyclopentadienyl derivatives of metals constitute an active field of research [1,2]. Reimer and Shaver [2] recently described the preparation of pentacarbonyl(η^1-pentachlorocyclopentadienyl)manganese, $Mn(\eta^1\text{-}C_5Cl_5)(CO)_5$ (I) from 2,3,4,5-tetrachlorodiazocyclopentadiene, $C_5Cl_4N_2$ and pentacarbonylchloromanganese, $Mn(CO)_5Cl$; the $C_5Cl_4N_2$ was made from perchlorocyclopentadiene in a multiple-step synthesis. In continuation of our studies on photoinduced reactions involving metal carbonyls [3] and also on reactions of perchlorocyclopentadiene with various metal carbonyls [4] we explored the possibility of synthesising $Mn(\eta^1\text{-}C_5Cl_5)(CO)_5$ (I) by a photochemical method, and describe below the synthesis of I direct from perchlorocyclopentadiene and $Mn_2(CO)_{10}$.

Experimental

All manipulations were carried out under dry nitrogen or argon and the solvents used were distilled and degassed before use. $Mn_2(CO)_{10}$ was obtained from Pressure Chemical Company, Pittsburgh, U.S.A., and used without further purification. Infrared spectra were recorded on a Perkin—Elmer Model 125 grating spectrophotometer. Mass spectra were recorded on a CH-5 Varian MAT mass spectrometer at 70 eV electron energies.

Synthesis of pentacarbonyl(η^1-pentachlorocyclopentadienyl)manganese, $Mn(\eta^1\text{-}C_5Cl_5)(CO)_5$

A mixture of 1.2 g (3.08 mmol) $Mn_2(CO)_{10}$ in a minimum volume of cyclohexane and 2.2 g (8.06 mmol) perchlorocyclopentadiene was irradiated for 12 h in a sealed Pyrex tube kept at a distance of about 20 cm from the UV-lamp. The tube was then cooled in liquid nitrogen and opened, and the evolved CO was pumped off through a vacuum line. The tube was then warmed to 0°C and the mixture was filtered. The filtrate was kept at —80°C for 6—8 h, and yellow crystals were obtained. These were dissolved in a minimum volume of pentane and the solution was filtered, then kept at —20°C to give 0.58 g (21% yield) of $Mn(\eta^1\text{-}C_5Cl_5)(CO)_5$ (I). M.p. 111°C. Analysis: Found: C, 27.87; Cl, 41.18. $C_{10}Cl_5O_5Mn$ calcd.: C, 27.78; Cl, 41.01%. Mass spectrum: 432$[M]^+$ 9.1%, 376 $[M - 2\ CO]^+$ 1.8%, 348 $[M - 3\ CO]^+$ 1.5%, 237 $[C_5Cl_5]^+$ 100%, 202 $[C_5Cl_4]^+$ 17.3%, 195 $[M - C_5Cl_5]^+$ 52.7%, 141 $[C_3Cl_3]^+$ 11.6%, 139 $[Mn(CO)_3]^+$ 3.1%, 130 $[C_5Cl_2]^+$ 11.2%, 111 $[Mn(CO)_2]^+$ 7.3%, 90 $[MnCl]^+$ 4.2%, 83 $[Mn(CO)]^+$ 9.1%, 55 $[Mn]^+$ 50.3%, 28 $[CO]^+$ 72.6%. IR spectrum (cm^{-1}): ring modes 1569vs, 1561w, 1258vs, 1191w, 1129s, 971vw, 948vw; C—Cl stretch 729s, 721w; ν(CO) 2071w, 2049vs, 2009s.

The other products isolated from the reaction include $Mn(CO)_5Cl$ (II) (Analysis: found: C, 26.12; Cl, 15.43; Mn, 23.81. C_5ClO_5Mn calcd.: C, 26.06; Cl, 15.39; Mn, 23.84%. Mass spectrum: 230 $[M]^+$ 17.1%, 174 $[Mn(CO)_3Cl]^+$ 12.2%, 102 $[MnCCl]^+$ 1%, 67 $[MnC]^+$ 4.6%, 55 $[Mn]^+$ 75.71%, 28 $[CO]^+$ 100%. IR (cm^{-1}): ν(CO) 2039m, 2051s, 1997vs), $C_{10}Cl_{10}$ (III) [5] (m.p. 123—124°C, Analysis: Found: C, 25.21; Cl, 74.71. $C_{10}Cl_{10}$ calcd.: C, 25.31, Cl, 74.69%. Mass spectrum: 475 $[M]^+$ 8.1%, 404 $[C_{10}Cl_8]^+$ 23.2%, 237 $[C_5Cl_5]^+$ 100%. IR (cm^{-1}): 1595vs, 1580(sh), 1250vs, 1180m, 1160s, 1010s, 970s, 950s, 810vs, 700vs, 670vw, 640s) and a small amount of $Mn_2(CO)_{10}$.

Results and discussion

All the isolated compounds were characterised by their elemental analysis, IR and mass spectral studies. The IR spectrum of I is in very good agreement with that previously reported [2].

The important features of the mass spectrum of I are the weak molecular ion peak at *m/e* 432 and the base peak at *m/e* 237 due to $[C_5Cl_5]^+$. Very weak peaks at *m/e* 376 and 348 are attributed to the fragment ions $[M - 2(CO)]^+$, and $[M - 3(CO)]^+$ and a relatively strong peak (52%) at *m/e* 195 is due to the ion $[M - C_5Cl_5]^+$. It is clear that under electron impact the molecule fragments rather readily; this is consistent with the observation by West et al. [6] that no molecular ion peak is present in the spectrum of the σ-bonded compound $Hg(C_5Cl_5)_2$. It appears that compound I mainly fragments to $[M - C_5Cl_5]^+$ and this is followed by decomposition of C_5Cl_5 and $Mn(CO)_5$ fragments. Very weak peaks at *m/e* 376 and 348 indicate that CO loss may compete to a small extent with C_5Cl_5 loss, but the loss of C_5Cl_5 should be favoured because the C_5Cl_5—Mn bond is a σ-bond whereas the metal—CO bonds involve both π- and σ-bonding.

The residue obtained from the reaction tube after washing with a small amount of dichloromethane followed by sublimation (40°C/0.1 mmHg) of the product gave the pale-yellow crystalline sublimate of $Mn(CO)_5Cl$ (II). A small amount of $Mn_2(CO)_{10}$ was obtained from the washings after drying and sublimation (50°C/0.8 mmHg). The combined residue left after separation of II and $Mn_2(CO)_{10}$ was extracted with dichloromethane to give the compound $C_{10}Cl_{10}$ (III). In view of the nature of the products I, II and III it is believed that the reaction most probably proceeds as follows:

$$Mn_2(CO)_{10} + C_5Cl_6 \rightarrow \underset{(I)}{(CO)_5Mn(C_5Cl_5)} + \underset{(II)}{Mn(CO)_5Cl}$$

Compound I then partially decomposes to $C_{10}Cl_{10}$ (III):

$$\underset{(I)}{2[(CO)_5Mn(C_5Cl_5)]} \rightarrow \underset{(III)}{C_{10}Cl_{10}} + \underset{(IV)}{Mn_2(CO)_{10}}$$

The fact, that the reaction gave no η^5-C_5Cl_5-manganese compound and that the dimer $[Mn(CO)_4Cl]_2$ could not be detected by IR and mass spectral studies, suggests that the radicals, $^{\cdot}Mn(CO)_5$, $^{\cdot}C_5Cl_5$, and $^{\cdot}Cl$ are formed, and then interact to give I, II, III and IV.

Acknowledgement

The author acknowledges the interest of Professor A. Haas of the Ruhr University at Bochum, West Germany in whose laboratory part of this work was conducted,

References

1 V.W. Day, B.R. Stults, K.J. Reimer and A. Shaver, J. Amer. Chem. Soc., 96 (1974) 4008.
2 K.J. Reimer and A. Shaver, Inorg. Chem., 14 (1975) 2707.
3 M.K. Chaudhuri, A. Haas and A. Wensky, J. Organometal. Chem., 116 (1976) 323.
4 M.K. Chaudhuri, Chem. and Ind., London submitted.
5 E.T. McBee, C.W. Roberts and J.D. Idol, Jr., J. Amer. Chem. Soc., 77 (1955) 4942.
6 G. Wulfsberg, R. West and V.N. Mallikarjuna Rao, J. Amer. Chem. Soc., 95 (1973) 8658.