Reaction of Cyclooctatetraenechromiumtricarbonyl with Dimethylacetylene Dimicarboxylate in Presence of Triirondodecacarbonyl—Exchange of Chromium by Iron & Contraction of Cyclooctatetraene Ring

S S ULLAH*, I AHMED, S E KABIR, M M KARIM & A H MOLLA
Department of Chemistry, Jahangirnagar University, Savar, Dhaka, Bangladesh

Received 1 March 1985; revised and accepted 24 June 1985

Metal exchange and ring contraction reactions occur when cyclooctatetraenechromiumtricarbonyl is refluxed for 1 hr with Fe₃(CO)₁₂ in the presence of dimethyl acetylenedicarboxylate in tetrahydrofuran under nitrogen atmosphere, as revealed by the formation of two complexes, viz. cyclooctatetraenetricarbonyl iron(I) (a metal exchange product) and (CO₉ CrC₆H₄(CO₂Me)₂ Fe(CO)₄(II) (a ring contraction product). The structures of the complexes have been established by spectral data (IR, PMR and mass) and elemental analyses.

The objective of the present work was to examine the reaction of cyclooctatetraenechromiumtricarbonyl with dimethyl acetylenedicarboxylate in the presence of Fe₃(CO)₁₂ and to identify the product(s) of this reaction. The product analysis revealed that the reaction took an unusual course in which the complex cyclooctatetraenechromiumtricarbonyl underwent metal exchange to give the known complex², cyclooctatetraeneirontricarbonyl(I) and another complex(II). The structures of the complexes(I) and (II) have been confirmed on the basis of spectral data (IR, PMR and mass) and elemental analyses.

Cyclooctatetraenechromiumtricarbonyl was prepared by the known procedure¹ by refluxing chromiumhexacarbonyl in acetonitrile and further refluxing this product in cyclooctatetraene (COT).

Reaction of cyclooctatetraenechromiumtricarbonyl with dimethyl acetylenedicarboxylate and triirondodecarbonyl

A mixture of cyclooctatetraenechromiumtricarbonyl (0.5g, 2.08 x 10⁻³ mol), dimethyl acetylenedicarboxylate (DMAD, 0.5g, 2.08 x 10⁻³ mol) and Fe₃(CO)₁₂ (1.05g, 2.08 x 10⁻³ mol) in tetrahydrofuran was refluxed for 1 hr under nitrogen atmosphere. Removal of solvent under reduced pressure afforded a solid mass which was extracted with pet ether (40-60°). The organic extract was chromatographed over a column of silica gel (60-120 mesh) employing pet ether (60-80°) as an eluent. Removal of solvent from eluate under reduced pressure gave rise to red crystals of the known² complex, COT Fe(CO₉) (complex-I) (0.417g, 82% based on cyclooctatetraenechromiumtricarbonyl), m.p. 93-95°; IR 2045, 1995 and 1985 em⁻¹ (CO); PMR (CDCl₃) : b 4.8 (s,8H); MS: m/z 244(M⁺), 216 (M-CO), 188 (M-2CO), 160 (M-3CO), 104 [M-(3CO+Fe)] and 78 (C₆H₆) (Found C,54.2; H, 5.5. Cl₁H₅Fe0₃ requires e, 54.1; H, 3.3%). The complex, COT Fe(CO₉) (I) was obtained in 90~10 yield by carrying out the reaction between COTCr(CO)₃ and Fe₃(CO)₁₂ in the absence of DMAD.

The second band on removal of solvent resulted in the isolation of a reddish yellow crystalline compound (complex II), 0.12g (10.48% based on cyclooctatetraenechromiumtricarbonyl), m.p. 142-45° (Found: e, 45.5; H, 2.5. Reqd: e, 45.3; H, 2.3%)

The structure of the complex (II) has been proposed on the basis of its spectral data (IR, PMR and mass) and elemental analyses. The complex (II) exhibited in its IR spectrum bands at 2060, 2040, 2015 and 1990 em⁻¹. Its PMR spectrum displayed three peaks at b 4.5 (s,5H), 8.5 (m,3H) and 7.5 (s,6H). The signal at b 4.5 is due to the protons of the aromatic moiety bonded to the Cr(CO₉) and that at b 8.5 (m,3H) is due to the sp³-protons of cyclobutene group coordinated to the Fe(CO)₄ group. The signal at b 7.5 has been attributed to the methyl protons of the ester groups. Its mass spectrum showed the parent molecular ion at m/z 556(M⁺) and other peaks at 219M⁻-C₁₂H₄O₆Fe), 336(M⁻-C₆H₅O₃). The mass spectrum also exhibited peaks due to successive loss of four CO units from the C₁₂H₄O₄ Fe group and three CO from the C₉H₄O₃ Cr group.

On the basis of the above spectral evidences we believe that the reaction between COTCr (CO)₃ and
DMAD in the presence of Fe₃(CO)₁₂ follows the pathway outlined in Scheme 1.

\[
\begin{align*}
\text{COT Cr(CO)₃} + \text{Fe(CO)₃} + \text{DMAD} & \rightarrow \text{COT Fe(CO)₃} + \text{Cr(CO)₃} \\
\text{Scheme 1}
\end{align*}
\]

The formation of COT Fe(CO)₃ by metal displacement is probably due to the greater stability as well as greater fluxional character of COT Fe(CO)₃ as compared to that of COT Cr(CO)₃. This is corroborated by the fact that when COT Cr(CO)₃ is reacted with Fe₃(CO)₁₂ in the absence of DMAD the product COT Fe(CO)₃ is obtained in near quantitative yield (90%). In the formation of complex(II) dimethyl acetylenedicarboxylate undergoes a Diels-Alder type of reaction with cyclooctatetraene to finally end-up in a cyclobutene moiety. The cyclobutene moiety is stabilized by an Fe(CO)₄ group supplied by Fe₃(CO)₁₂ to give the complex (II) in 26% yield. In the reaction Scheme 1, metal exchange reaction predominates over the ring contraction reaction as is evident from the yields of the complexes(I) and (II).

The authors are thankful to Mr. Alauddin Ahmed, Department of Chemistry, Tohoku University, Japan, for the IR, PMR and mass spectra and elemental analyses.

References