Tetrahedron Letters No. 13, pp. 444-447, 1961. Pergamon Press Ltd. Printed in Great Britain.

MIXED π-HYDROCARBONMETAL CARBONYL DERIVATIVES*

M. Cais and M. Feldkimel

Department of Chemistry, Israel Institute of

Technology, Haifa, Israel

(Received 26 June 1961)

SOME of the research attempts in our laboratory have been directed towards the synthesis of organometallic π-complexes incorporating two or more metallic atoms in the same molecule. In the preceeding communication[1] we have described several such compounds whose synthesis was based on the benzene-like, aromatic properties of the cyclopentadienyl ring in metallocenes.

We now wish to report some results of a different approach to the synthesis of multiple-metal π-complexes of organic molecules.

The displacement of CO groups of metal carbonyls by hydrocarbon ligands has been shown to take place in a variety of cases.[2] The reaction of butadiene with iron pentacarbonyl first described in 1930,[3] has been recently reinvestigated[4] and it has been shown that the resulting compound is the π-complex butadieneiron tricarbonyl.

---

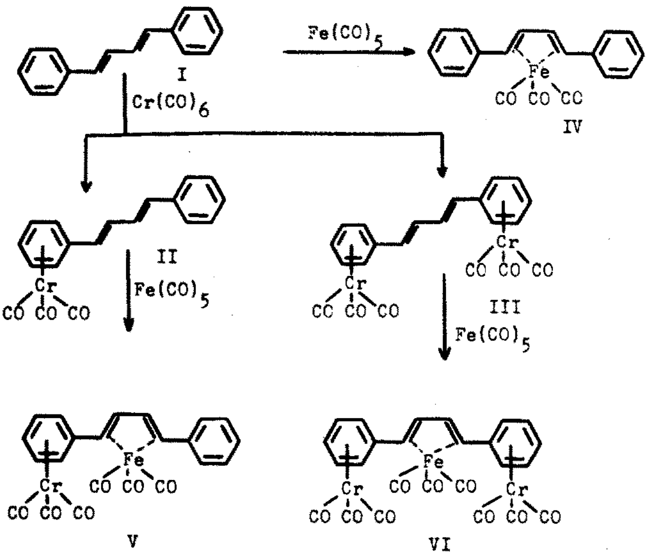
[*] Organometallic Studies - V.

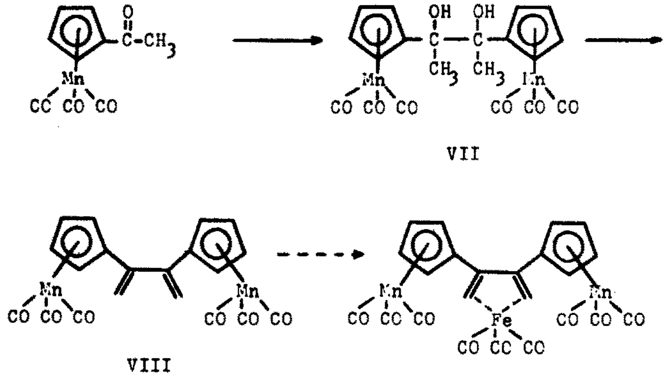
[1] Part IV: M. Cais and M. Feldkimel, Tetrahedron Letters No. 13, 440 (1961), preceding paper.

[2] For a recent review see Chapters 8 and 10 in H. Zeiss (Editor), Organometallic Chemistry. Reinhold, New York (1960).

[3] H. Reihlen, A. Gruhl, G. Hessling and O. Pfrengle, Liebigs Ann. 482, 161 (1930).

[4] B.F. Hallam and P.L. Pauson, J.Chem.Soc. 642 (1958).





Similarly several authors[5-7] have shown independently that the metal carbonyls react readily with aromatic systems to form arene-carbonylmetal

---

[5] E.O. Fischer and K. Ofele, Chem.Ber. 90, 2532 (1957).

[6] G. Natta, R. Ercoli and F. Calderazzo, Chim. e Ind. 40, 287 (1958).

[7] M.C. Whiting and B. Nicholls, J.Chem.Soc. 551 (1959).

complexes.

We have combined the above two reactions to obtain novel compounds of the type described below. For example, when 1,4-diphenylbutadiene (I) was reacted with chromium hexacarbonyl, we isolated two compounds: 1-(phenylchromium tricarbonyl)-4-phenylbutadiene (II) (60% yield), orange-red crystals, m.p. 150-152° (Found: C, 66.69; H, 4.22; Cr, 16.00. $C_{19}H_{14}CrO_3$ requires: C, 66.66; H, 4.12; Cr, 15.2%); and a small amount of 1,4-di-(phenylchromium tricarbonyl)butadiene (III), red crystals, m.p. 174-176° (Found: C, 55.51; H, 2.85; Cr, 21.80. $C_{22}H_{14}Cr_2O_6$ requires: C, 55.24; H, 2.95; Cr, 21.75%). Compound (III) was obtained in over 50% yield when (II) was reacted again with chromium hexacarbonyl. All three compounds, (I), (II) and (III) were then reacted with iron pentacarbonyl to give respectively 1,4-diphenylbutadieneiron tricarbonyl (IV), yellow orange crystals, m.p. 165-166° (Found: C, 65.82; H, 4.10. $C_{19}H_{14}O_3Fe$ requires: C, 65.92; H, 4.07%); 1-(phenylchromium tricarbonyl)-4-phenyl-butadieneiron tricarbonyl (V) m.p. 186-188° (dec.) (Found: C, 55.04; H, 2.98. $C_{22}H_{14}O_6CrFe$ requires: C, 54.80; H, 2.92%) and 1,4-di(phenylchromium tricarbonyl)butadieneiron tricarbonyl (VI), m.p. 191-193° (dec.)(Found: C, 48.36; H, 2.27. $C_{25}H_{14}O_9Cr_2Fe$ requires: C, 48.57; H, 2.28%).

The same series of reactions was carried out with 1-phenylbutadiene and work is currently in progress to extend these reactions to other systems containing both arene and conjugated diene moieties in the same molecule.

As an example of such an extension we wish to mention the preparation of the pinacol (VII), yellow crystals, m.p. 163-165° (Found: C, 48.82; H, 3.14; Mn, 22.24. $C_{20}H_{14}H_8Mn_2$ requires: C, 48.56; H, 3.26; Mn, 22.23) and its dehydration to the substituted butadiene (VIII), yellow crystals, m.p. 116-117° (Found: C, 52.69; H, 2.75; Mn, 24.22. $C_{20}H_{12}O_6Mn_2$ requires C, 52.43; H, 2.64; Mn, 23.98%). The reaction of VIII with iron pentacarbonyl is under investigation.

The infra-red spectra and ultra-violet spectra of the new compounds have been measured and details will be published in the full paper.

We wish to thank the Israeli Ministry of Commerce and Industry for financial support and Ethyl Corporation, Detroit, Mich., U.S.A., for generous samples of metal carbonyls.