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

ORGANOMETALLIC π-COMPLEXES
XX*. THE PREPARATION OF STYRENETRICARBONYLCHROMIUM

M. D. RAUSCH, G. A. MOSER, E. J. ZAIKO AND A. L. LIPMAN, JR.**
Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, 01002 (U.S.A.)

(Received December 1st, 1969)

SUMMARY

The reaction of styrene and triamminetricarbonylchromium in refluxing dioxane gives styrenetricarbonylchromium in 50–65% yield. The complex can also be synthesized in 83% yield via a Wittig reaction involving benzaldehydetricarbonylchromium. Catalytic hydrogenation of styrenetricarbonylchromium produces ethylbenzenetricarbonylchromium, which has likewise been prepared directly from ethylbenzene and triamminetricarbonylchromium. Spectral properties and polymerization reactions of styrenetricarbonylchromium are discussed.

INTRODUCTION

Because of the great importance of the chemistry of styrene, we have been interested for some time in the possible formation, properties, and reactions of the corresponding arene–metal π-complex, styrenetricarbonylchromium (I). Although many arenetricarbonylchromium derivatives are known in the literature[2], the styrene complex (I) has not yet, to our knowledge, been described. Coordination of the π-electrons in the benzene ring of styrene might be expected to exert a noticable influence on the reactivity of the *exo*-cyclic double bond. For example, Pettit and coworkers[3] have recently shown that the solvolysis of (benzyl chloride)tricarbonylchromium proceeds ca. 10^5 times faster than does the solvolysis of benzyl chloride itself, indicating a marked effect on the part of the $Cr(CO)_3$ substituent in this process.

A number of organometallic compounds containing styrene are known. However, most of these are palladium or platinum derivatives in which the double bond of styrene is coordinated to the metal in the form of a metal–olefin π-complex[4–9]. Stone and coworkers failed to isolate any iron π-complexes from the reaction of styrene and $Fe_3(CO)_{12}$, although reactions of the latter with either *m*- or *p*-divinylbenzene produced products in which it was postulated that four of the six ring π-electrons, in addition to the vinylic π-electrons, were involved in metal coordination[10].

---

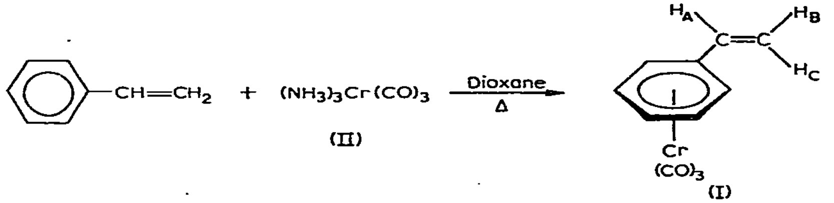
* For Part XIX see ref. 1.
** National Science Foundation Undergraduate Research Participant, Summer, 1966.

RESULTS AND DISCUSSION

Initial attempts to synthesize (I) directly from chromium hexacarbonyl and styrene by methods analogous to those described by Nicholls and Whiting[11] were unsuccessful. The reaction was run in diglyme, 2-picoline, and in excess styrene as the solvent. In all runs, polystyrene together with green chromium salts were formed. The polymers were identified by their characteristic IR spectra, and the spectra were devoid of absorptions in the usual metal–carbonyl region. Although the tert-butylpyrocatechol inhibitor was left in the styrene during these reactions to restrict polymerization as much as possible, the inhibitor was apparently rendered ineffective under the conditions employed.

In subsequent studies, we decided to investigate the use of the reagent triamminetricarbonylchromium (II) in the potential synthesis of (I). Reagent (II) has been used successfully in our earlier synthesis of (7-chloronorbornadiene)tetracarbonylchromium[12] and was also used by Kaesz and coworkers[13] in their preparation of cyclooctatetraenetricarbonylchromium. We have developed a facile synthesis for (II), which is much more convenient than the original method of Hieber *et al.*[14] and which produces (II) in yields of 90–99%.

A reaction between (II) and styrene in refluxing dioxane has been found to produce styrenetricarbonylchromium (I) in 50–65% yield*. The product can be purified by chromatography or recrystallization from hexane, both preferably under nitrogen, or by vacuum sublimation. Styrene complex (I) is reasonably stable in the crystalline state in air at room temperature, but solutions of (I) in organic solvents are somewhat air-sensitive. The IR spectrum of (I) (KBr disc) exhibited a medium-intensity peak at 3090 cm^{-1}, assignable to vinylic and/or aromatic C–H stretching frequencies, two very strong peaks at 1960 and 1870 cm^{-1} (shoulder at 1890 cm^{-1}), indicative of a $M(CO)_3$ group, a medium-intensity peak at 1633 cm^{-1}, assignable to a C=C stretcing frequency, medium-intensity bands at 1410 and 1290 cm^{-1} which can be attributed to vinylic C–H in-plane bending vibrations, and peaks at 995, 985, 930 and 920 cm^{-1} in the vinylic C–H out-of-plane bending region. Absorption in the aliphatic C–H stretching region was absent, indicating that the product was monomeric. A monomeric structure was also indicated by a molecular weight measurement in benzene solution. A detailed study of the mass spectra of (I) and certain deuterated derivatives is currently in progress[15].



The proton NMR spectrum of (I) in $CDCl_3$ solution is also in accord with the proposed structure. When determined at 60 MHz, a one-proton quartet centered

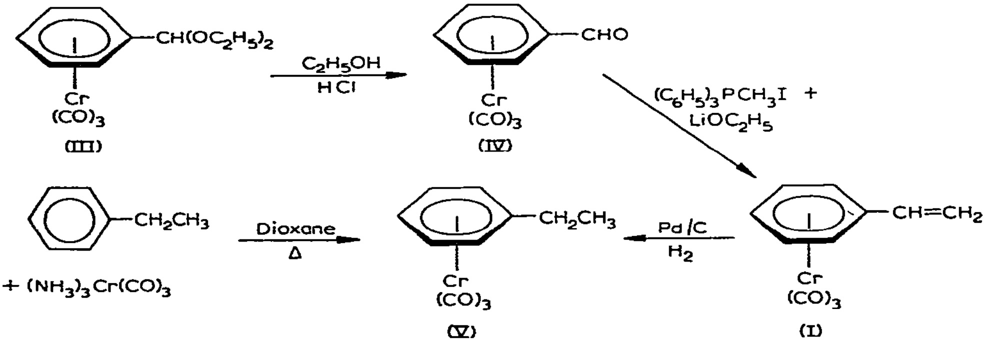
---

* Triamminetricarbonylchromium (II) appears to be a very useful intermediate for the synthesis of arenetricarbonylchromium complexes, since reactions of it with biphenylene, dibenzobarrelene, tert-butylbenzene, thiophene, etc., give very good yields of the corresponding tricarbonylchromium derivatives[24].

at τ 3.68 and assignable to H_A is clearly observable, while resonances due to the remaining seven protons (H_B, H_C, H_{Ar}) occur as an apparent singlet at τ 4.23 and a multiplet centered at τ 4.60. The 100 MHz spectrum of (I) is very similar, except that a one-proton doublet (J_{AC} 18 Hz) attributable to H_C is now also clearly distinguishable. The resonance at τ 4.23 in the 60 MHz spectrum thus represents one-half of the H_C doublet while the other half of the doublet occurs with resonances due to H_B and H_{Ar}. The aromatic protons of styrene* are therefore shifted upfield by ca. 1.9 ppm upon complexation with the $Cr(CO)_3$ moiety, and the magnitude of this shift is essentially the same as has been observed for the complexation of benzene by this group[17]. The vinylic proton H_A is shifted upfield by ca. 0.4 ppm, while the H_B and H_C protons are virtually unaffected by the $Cr(CO)_3$ group.

Öfele[18] has recently described a convenient method for the synthesis of arenetricarbonylchromium complexes in which a reaction between the arene and tris(4-picoline)tricarbonylchromium is promoted by boron trifluoride dimethyl etherate. In order to determine if the addition of a Lewis acid would facilitate the formation of (I), several experiments were conducted in which anhydrous zinc chloride was added to the mixture of styrene and (II) in refluxing dioxane. Product formation under these conditions appeared to be complete in only one to five minutes; however, the yield of (I) proved to be substantially reduced (11–17%).

A second route to (I) has involved a Wittig reaction between benzaldehydetricarbonylchromium (IV) and triphenylmethylenephosphorane, utilizing the general procedure of Drehfahl *et al.*[19]. Styrene complex (I) was prepared in 83% yield by this procedure. The benzaldehyde complex (IV) was obtained by the acidic hydrolysis of (benzaldehyde diethyl acetal)tricarbonylchromium (III), which in turn was prepared in good yield from a reaction between (II) and benzaldehyde diethyl acetal in refluxing dioxane. The m.p. of (IV) has been reported by Drehfahl *et al.*[19] to be 78.5–79.5° and by Mostardini *et al.*[20] to be 46.5–47.5°; our value of 78.5° for the m.p. of (IV) is in agreement with the former workers. The catalytic hydrogenation of (I) proceeded smoothly to afford ethylbenzenetricarbonylchromium (V) in 52% yield. The latter product was shown to be identical to (V) prepared directly from ethylbenzene and (II).



Preliminary studies suggest that (I) undergoes polymerization reactions less readily than does styrene itself. Thus, an attempted polymerization of (I) in toluene

---

* Proton NMR spectra data for styrene in $CDCl_3$ solution have been previously given[16]. The chemical shift value stated for H_A in ref. 16 is unfortunately in error; the correct value should be τ 3.25.

solution at 100° using azobisisobutyronitrile (AIBN) as a free-radical initiator produced no polymer, and resulted in a ca. 70% recovery of starting material. Under these same conditions, styrene is readily polymerized[21]. Attempted thermal polymerization of (I) at 115° under nitrogen, either in the presence or absence of AIBN, also appeared to be unsuccessful, and only greenish, metallic-like residues which were insoluble in common organic solvents could be isolated. However, when equal amounts of (I) and styrene were heated together at 100° for a 6 h period, a product believed to be a copolymer of (I) and styrene was obtained. When this product was subsequently heated at 70° *in vacuo* for an 8 h period, no sublimate was observed, indicating the absence of unreacted (I). An IR spectrum of the product was very similar to the spectrum of polystyrene, with the exception of two very intense bands in the terminal carbonyl region and several bands of weak to medium intensity at lower frequencies. No absorption bands were present in the region near 1633 cm^{-1}, again indicating the absence of monomer (I).

Additional reactions of (I) are currently in progress and will be described at a later date.

EXPERIMENTAL SECTION

Proton NMR spectra were recorded on a Varian A-60 spectrometer, and IR spectra were obtained on a Beckman IR-10 spectrophotometer. Melting points were determined in air and are uncorrected. Elemental analyses were performed by Mr. Charles Meade of the Microanalysis Laboratory, Office of Research Services, University of Massachusetts. All reactions were run under an atmosphere of nitrogen. Styrene and ethylbenzene were obtained commercially and were used without further purification; the tert-butylpyrocatechol inhibitor in the styrene was not removed before use. Methyltriphenylphosphonium iodide was prepared according to a literature method[22], while lithium ethoxide was prepared by the direct reaction of lithium metal and absolute ethanol.

Reaction of styrene and chromium hexacarbonyl

Chromium hexacarbonyl (1.1 g, 5.0 mmoles) and styrene (8.2 ml, 72 mmoles) were placed in a 100-ml flask which had been repeatedly flushed with nitrogen. The reactants were heated to reflux for 1 h, during which time the solution turned yellow, then orange, and a viscous liquid was obtained. Following the addition of 100 ml of ethyl ether, the reaction mixture was filtered through alumina. Both the resulting yellow solution and the viscous mass which remained on the alumina were separately dissolved in toluene and cast into films by evaporating the toluene on a hot plate. IR spectra taken on both films identified them as polystyrene; absorptions in the terminal carbonyl region were absent.

Triamminetricarbonylchromium (II)[14]

Chromium hexacarbonyl (4.5 g, 20.4 mmoles) and a solution of 7.75 g of potassium hydroxide in 120 ml of 95% ethanol were placed in a 200-ml pressure bottle. The bottle was filled with nitrogen and capped with a mechanical capper. The pressure bottle was wrapped in cloth and placed in a steam bath for 6 h. After this time the bottle was cooled in ice and opened carefully. The orange solution was poured under nitrogen into a 1-l flask. The bottle was washed with 30 ml of concentrated ammonium hydroxide and the washings were added to the flask. Subsequently, 120 ml of ammonium hydroxide was added to the flask and the mixture stirred for 2 h under a nitrogen atmosphere. During this period the solution turned bright yellow. The yellow crystals were filtered under nitrogen using a glass frit; decompn. 100–105° (N_2). The yield of (II) was 3.52 g (93%). Complex (II) can be conveniently weighed in air, but is best stored for extended periods under nitrogen.

Styrenetricarbonylchromium (I)

Into a 100-ml round-bottomed flask, fitted with a nitrogen inlet tube, a magnetic stirring bar, and a condenser equipped with a mercury check valve, were placed 1.00 (5.35 mmoles) of triamminetricarbonylchromium, 0.50 ml (0.46 g, 4.4 mmoles) of styrene and 25 ml of dioxane. The reaction mixture was heated to reflux for 2½ h and then cooled in an ice bath. During the cooling period, a slight positive flow of nitrogen was maintained. The cooled reaction mixture was filtered under nitrogen through a glass frit (25–50 μ) to give an orange solution. The solvent was removed under reduced pressure and the solid which remained was sublimed (65°, 0.05 mm Hg) in a water-cooled, cold-finger sublimer to yield 0.655 g (62%) of orange crystals of (I), m.p. 78–79°. An analytical sample of m.p. 80–81° was prepared by recrystallization of the product from hexane under nitrogen. (Found: C, 55.00; H, 3.40; Cr, 21.6; mol.wt. osmometric in benzene, 250. $C_{11}H_8CrO_3$ calcd.: C, 55.01; H, 3.36; Cr, 21.65%; mol.wt., 240.)

Terminal carbonyl stretching frequencies for (I) in cyclohexane solution were observed at 1980 and 1913 cm^{-1}.

Direct synthesis of ethylbenzenetricarbonylchromium (V)

In a manner similar to that described above, 1.00 g (5.35 mmoles) of triamminetricarbonylchromium, 3.00 ml (2.60 g, 24.5 mmoles) of ethylbenzene and 25 ml of dioxane were heated to reflux for 4 h. Filtration, followed by removal of the solvent under reduced pressure, yielded a yellow solid. After sublimation of the product at 70°/0.05 mm, 1.10 g (86%) of yellow crystals of (V), m.p. 38–39°, were isolated. (Found: C, 54.45; H, 4.16; Cr, 21.8. $C_{11}H_{10}CrO_3$ calcd.: C, 54.55; H, 4.16; Cr, 21.47%.)

The NMR spectrum ($CDCl_3$ soln.) of (V) exhibited an aromatic proton multiplet (intensity 5) centered at τ 4.72, a quartet (J 7 Hz) at τ 7.66, intensity 2, attributed to the methylene protons, and a triplet (J 7 Hz) at τ 8.78, intensity 3, attributed to the methyl protons.

Catalytic hydrogenation of styrenetricarbonylchromium (I)

Into a 125-ml filter flask were added 0.200 g (0.833 mmole) of styrenetricarbonylchromium, 1.00 g of palladium-on-charcoal catalyst, a magnetic stirring bar, and 50 ml of nitrogen-saturated ethyl acetate. The flask was flushed with hydrogen via an inlet tube. After several min, a balloon was attached to the side arm of the flask, and was inflated to its capacity. At this point, the hydrogen inlet tube was sealed, and the reaction mixture was allowed to stir for 24 h. The solution was filtered under nitrogen to remove the catalyst and the yellow filtrate was evaporated to dryness. Sublimation of the residue at 65°/0.05 mm produced 0.105 g (52%) of yellow crystalline (V), m.p. 38.5°. A mixture m.p. determination with a sample of (V) prepared above was undepressed.

Benzaldehyde diethyl acetal

A modification of a literature procedure was used[23]. A mixture of benzaldehyde (11.0 g, 0.104 mole), ethyl orthoformate (15.1 g, 0.102 mole) and 2 drops of concn. sulfuric acid was allowed to stir at room temperature for 24 h, after which time 0.20 g of sodium carbonate was added to neutralize the solution. Filtration, followed by distillation at reduced pressure yielded 11.75 g (64%) of benzaldehyde diethyl acetal, b.p. 96–99°/11–15 mm (lit.[23] 222°/760 mm).

(Benzaldehyde diethyl acetal)tricarbonylchromium (III)

Benzaldehyde diethyl acetal (1.0 g, 5.5 mmoles) and triamminetricarbonylchromium (1.00 g, 5.35 mmoles) were heated under nitrogen for 5 h in 25 ml of refluxing dioxane. At the end of this period, a positive flow of nitrogen was begun and the reaction mixture was cooled in ice. Filtration under nitrogen through a glass frit gave an orange-yellow solution. The latter was concentrated to *ca.* 1 ml and subjected to column chromatography (Merck neutral grade alumina; 16.5 by 1.5 cm). The column was first eluted with 75 ml of hexane. A yellow band which remained near the top of the column was removed by elution with dichloromethane. Concentration of the yellow solution to 1 ml and the addition of 2 ml of hexane produced, after cooling in a freezer and filtration, 1.25 g (74%) of (III), m.p. 49° (lit.[19] 53–54°). (Found: C, 53.17; H, 5.10; Cr, 16.5; O, 25.30. $C_{14}H_{16}CrO_5$ calcd.: C, 53.17; H, 5.10; Cr, 16.44; O, 25.29%.)

The NMR spectrum ($CDCl_3$ soln.) of (III) exhibited a multiplet centered at τ 4.57, intensity 6, attributed to the methine and aromatic protons, a quartet (J 7 Hz) at τ 6.35, intensity 4, attributed to the methylene protons, and a triplet (J 7 Hz) at τ 8.77, intensity 6, attributed to the methyl protons.

Benzaldehydetricarbonylchromium (IV)

In a manner similar to that described in the literature[19], hydrolysis of (benzaldehyde diethyl acetal)tricarbonylchromium in nitrogen-saturated ethanolic HCl produced red crystals of (IV), m.p. 78.5° (lit.[19] m.p. 78.5–79.5°), in 89% yield.

The NMR spectrum ($CDCl_3$ soln.) of (IV) exhibited a sharp singlet at τ 5.25, intensity 1, attributed to the aldehydic proton, and a multiplet centered at τ 7.17, intensity 5, attributed to the aromatic protons.

Preparation of styrenetricarbonylchromium (I) from benzaldehydetricarbonylchromium (IV)

Into a stirred solution of methyltriphenylphosphonium iodide (1.21 g, 2.99 mmoles) and 50 ml of absolute ethanol was added dropwise a solution of lithium ethoxide (0.13 g, 2.5 mmoles) in 50 ml of absolute ethanol. The reaction mixture was allowed to stir for 4 h, after which time benzaldehydetricarbonylchromium (0.050 g, 0.21 mmole) in 25 ml of absolute ethanol was added dropwise over a 25 min period. After an additional 8 h of stirring at room temperature, the orange reaction mixture was concentrated to *ca.* 4 ml under reduced pressure, and subjected to column chromatography (Merck neutral grade alumina; 16.5 by 1.5 cm) under nitrogen.

Elution with hexane resulted in an orange-yellow solution. Evaporation of the solvent under reduced pressure followed by sublimation of the resulting residue produced 0.041 g (83%) of styrenetricarbonylchromium (I), m.p. 78–79°.

Thermal co-polymerization of styrene and styrenetricarbonylchromium (I)

Styrene (0.400 g, 3.85 mmoles) and styrenetricarbonylchromium (0.400 g, 1.66 mmoles) were heated to 100° for 6 h in a small Schlenk tube under a nitrogen atmosphere. The reaction vessel was cooled and 4 ml of dry, nitrogen-saturated benzene was added. After stirring, the reaction product dissolved to give a light olive-colored solution. Nitrogen-saturated methanol (*ca.* 12 ml) was added and a solid precipitated. The solvent was removed under reduced pressure yielding 0.47 g of an olive-colored solid. A portion of this product was subjected to sublimation conditions under which styrenetricarbonylchromium is known to sublime; no trace of starting complex (I) was detected.

An IR spectrum (KBr disc) of the olive-colored solid exhibited the following bands, in addition to the band normally observed in the spectrum of polystyrene: 1970 cm^{-1} and 1885 cm^{-1} (broad), both strong and attributed to terminal metal carbonyl stretching modes; weak to medium intensity absorptions at 1427, 1265, 814, 660, 631 (low energy shoulder), and 486 cm^{-1}.

ACKNOWLEDGEMENTS

The authors are very grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this research program. They are also indebted to Dr. Peter West of the Dow Chemical Co. for determination of the 100 MHz NMR spectrum of (I), and to Dr. R. Lenz for helpful discussions concerning the polymerization experiments.

REFERENCES

1 M. D. Rausch and G. C. Schloemer, *Org. Prep. Proc.*, 1 (1969) 131.
2 H. Zeiss, P. Wheatley and H. Winkler, *Benzenoid-Metal Complexes*, Ronald Press, New York, N.Y., 1966, Chapt. 3.
3 J. D. Holmes, A. K. Jones and R. Pettit, *J. Organometal. Chem.*, 4 (1965) 324.
4 M. S. Kharasch and T. A. Ashford, *J. Amer. Chem. Soc.*, 58 (1936) 1733.
5 J. S. Anderson, *J. Chem. Soc.*, (1936) 1042.
6 A. D. Hel'man, *C. R. Acad. Sci. URSS*, 16 (1937) 351; *Chem. Abstr.*, 32 (1938) 2081.
7 M. S. Kharasch, R. C. Seyler and F. R. Mayo, *J. Amer. Chem. Soc.*, 60 (1938) 882.
8 W. M. MacNevin and S. A. Giddings, *Chem. Ind. (London)*, (1960) 1191.
9 J. R. Holden and N. C. Baenziger, *J. Amer. Chem. Soc.*, 77 (1965) 4897.
10 T. A. Manuel, S. L. Stafford and F. G. A. Stone, *J. Amer. Chem. Soc.*, 83 (1961) 3597.
11 B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, (1959) 551.
12 D. F. Hunt, C. P. Lillya and M. D. Rausch, *Inorg. Chem.*, 8 (1969) 446.
13 C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz and S. Winstein, *J. Amer. Chem. Soc.*, 88 (1966) 3444.
14 W. Hieber, W. Abeck and H. K. Platzer, *Z. Anorg. Allg. Chem.*, 280 (1955) 252.
15 M. M. Bursey, F. E. Tibbetts, W. F. Little, M. D. Rausch and G. A. Moser, *Tetrahedron Lett.*, (1969) 3469; unpublished studies.
16 M. D. Rausch and A. Siegel, *J. Organometal. Chem.*, 11 (1967) 317.
17 W. McFarlane and S. O. Grim, *J. Organometal. Chem.*, 5 (1966) 147.
18 K. Öfele, *Chem. Ber.*, 99 (1966) 1732.

19 G. DREHFAHL, H. H. HÖRHOLD AND K. KÜHNE, *Chem. Ber.*, 98 (1965) 1826.
20 E. MOSTARDINI, F. CALDERAZZO AND R. ERCOLI, *Chim. Ind. (Milan)*, 42 (1960) 1231.
21 W. R. SORENSON AND T. W. CAMPBELL, *Preparative Methods of Polymer Chemistry*, Interscience, New York, N.Y., 1961, p. 162.
22 K. FRIEDRICH AND H. G. HENNING, *Chem. Ber.*, 92 (1959) 2756.
23 H. W. POST, *J. Org. Chem.*, 5 (1940) 244.
24 G. A. MOSER AND M. D. RAUSCH, unpublished results.