

COORDINATION SYNTHESIS ON METAL CENTERS

III*. PREPARATION AND REACTIONS OF VINYLCHROMIUM

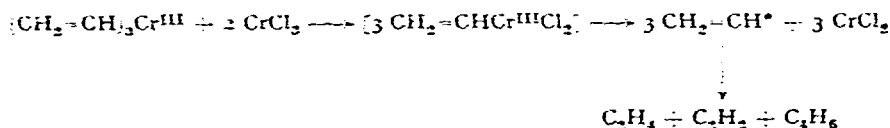
H. P. THRONDSSEN, W. METLESICS** AND H. ZEISS

Monsanto Research S.A., Zurich (Switzerland)

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In analogy with earlier work devoted to the preparation of σ - and π -bonded organochromium compounds^{1,2}, the present work is concerned with the reactions of chromium(III) chloride as its tetrahydrofuranate with vinylmagnesium chloride in various molecular ratios in tetrahydrofuran. It was anticipated that under carefully controlled reaction conditions σ -bonded vinylchromium compounds would be formed.

The addition of vinylmagnesium chloride³ to either a suspension of anhydrous chromium trichloride or chromium trichloride tristetrahydrofuranate in tetrahydrofuran at -70° in equimolecular ratios results in the reduction of chromium(III) to chromium(II) and the formation of butadiene, ethylene and some acetylene. Chromium(II) chloride, which separates from the solution as its tetrahydrofuranate, was characterized and identified as the bipyridyl complex, $[(bipy)_3Cr](ClO_4)_2$. In the absence of isolable intermediates any mechanistic proposal is speculative. However, one explanation, based upon the assumption that the initial reaction gives solvated trivinylchromium, lies in the following interpretation for these findings.



During the reaction of three equivalents of vinylmagnesium chloride with one of chromium trichloride tristetrahydrofuranate at -78° in tetrahydrofuran the Gilman color test remains positive. At a temperature between -60 and -50° the reaction goes to completion (negative Gilman test); however, it is accompanied by the formation of small quantities of butadiene and ethylene in approximately equal molar ratios. The final reaction mixture was hydrolyzed and the products were shown to consist of additional butadiene and ethylene. No bis-arene- π -complex or benzene was detected.

The formation of ethylene from this reaction indicates the existence, at low temperatures, of an unstable organochromium compound. In order to prove the existence of such a compound the reaction mixture was deuterolyzed at -60 to -50° , and monodeuteroethylene, identified by its infrared spectrum, was isolated in low

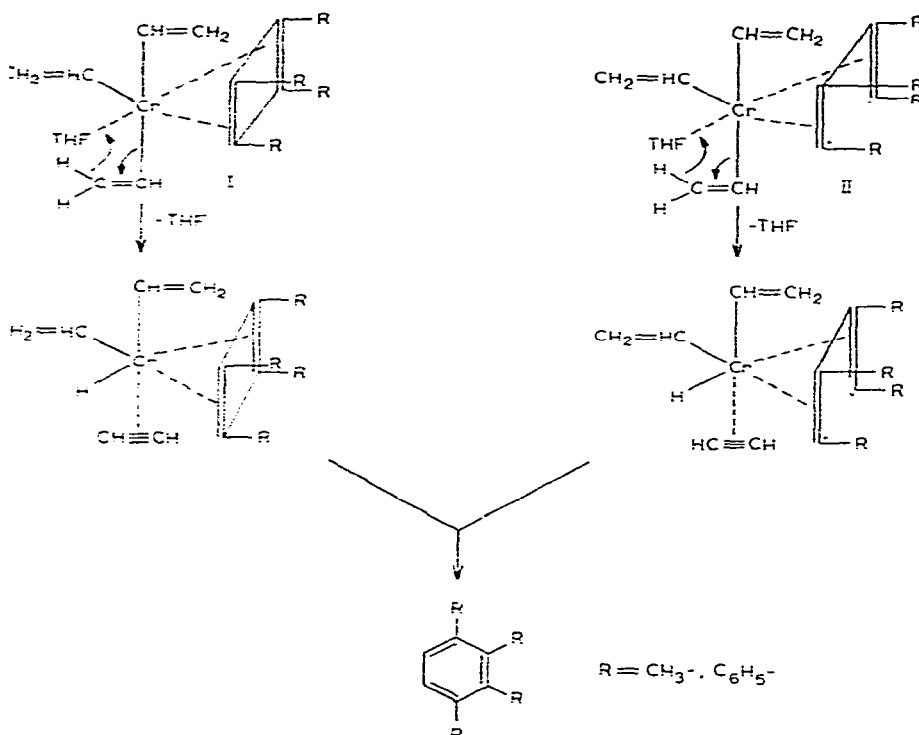
* For Part II, see ref. 10.

** Present address: Hoffmann-La Roche, Nutley, N.J., U.S.A.

yields. The presence of a monodeuteroethylene indicates that there is a σ -bonded vinylchromium compound in solution, and, since all the vinylmagnesium chloride has been consumed, the intermediate may be a solvated trivinylchromium.

A further indication for the existence of a solvated vinylchromium compound was found in the reaction between vinylmagnesium chloride and chromium trichloride di-tetrahydrofuranate (molar ratio, 3:1) with disubstituted acetylenes. It is known⁴ that, in the reaction of triorganochromium compounds with disubstituted acetylenes, at least two types of products can be formed. These include trimerization products of acetylenes giving hexasubstituted benzene derivatives and products in which two molecules of acetylene combine with one of the groups attached to chromium with concomitant hydrogen abstraction.

On reaction of diphenylacetylene and dimethylacetylene in tetrahydrofuran with the vinylmagnesium chloride*-chromium(III) chloride system at low temperatures, followed by warming the mixture to room temperature, trimerization of the



acetylenes occurs with the formation of hexaphenylbenzene or hexamethylbenzene, respectively. Furthermore, 1,2,3,4-tetraphenylbenzene and 1,2,3,4-tetramethylbenzene can be isolated from these reactions. In the reaction with diphenylacetylene, *ans*-stilbene was also isolated.

It has been proposed⁶ that the tetrasubstituted benzene derivatives arise by interaction of two acetylene molecules coordinated to chromium in the form of a

* It has earlier been shown⁵ that vinylmagnesium chloride fails to react with disubstituted acetylenes.

tetrasubstituted cyclobutadiene complex (I) or a tetrasubstituted butadiene diradical⁷. In the present reactions the observed products can arise by the interaction of one of the vinyl groups attached to chromium, within such a complex, with concomitant hydrogen abstraction.

EXPERIMENTAL

(with Mr. P. RÜESCH)

All experiments involving organometallic compounds were carried out under pure, dry nitrogen. The tetrahydrofuran used was freshly distilled from lithium aluminum hydride. Vinyl chloride (purity 99.9%) was taken from a gas cylinder. The chromium trichloride tristetrahydrofuranate was prepared as reported elsewhere⁸. The vinyl Grignard reagent was prepared in tetrahydrofuran in accordance with the literature³. The concentrations of the vinylmagnesium chloride solutions were estimated by acid-base titrations using a Beckman pH-meter.

Analysis of the vinylmagnesium chloride solution

An aliquot of the vinylmagnesium chloride solution was hydrolyzed at 0° with deoxygenated water. The gaseous material collected was shown by means of infrared and vapor phase chromatographic techniques to be only ethylene.

Ratio of 1:1 of chromium(III)chloride and vinylmagnesium chloride

A solution (20 ml) of vinylmagnesium chloride (4.53 g, 0.0523 mole) was added to a stirred suspension of chromium trichloride tristetrahydrofuranate (19.56 g, 0.0523 mole) in tetrahydrofuran (100 ml) at -70°. The resulting reaction mixture was slowly warmed to room temperature, reaction commenced at about -50° as indicated by a color change to dark brown. During the reaction a white material was formed concurrent with gas evolution (gaseous material was collected at -126° using a liquid nitrogen-methylcyclohexane mixture).

(a) *Isolation of chromium(II)chloride.* After 2.5 h the white solid formed was removed by filtration under nitrogen and washed several times with cold tetrahydrofuran and finally dried in vacuo. The white solid, chromium(II)chloride tetrahydrofuranate, was dissolved in air-free water and treated with an excess of 2,2'-bipyridyl in methanol and dilute (5%) deoxygenated perchloric acid. The black complex $[(bipy)_2Cr^+(ClO_4)_2]$ crystallized from the violet solution and was washed with cold, air-free methanol. An X-ray powder photograph of this material was identical with an authentic specimen.

The brown filtrate from the separation of chromium(II) chloride was hydrolyzed with water. An unidentified yellow oil was isolated from the organic extract.

(b) *Analysis of the gaseous material.* The gaseous material was transferred into a vacuum apparatus and by vacuum distillation between traps at various temperatures (-78°, -126°, -195°) three fractions were separated. (i) Tetrahydrofuran, vapor pressure of 52 mm at 0° was collected in the trap at -78°. (ii) Butadiene (299 mg, 5.55 mmoles), vapor pressure of 11 mm at -78°, further identified by comparison of its IR-spectrum with an authentic sample, was collected in the trap at -126° together with an unknown gas. (iii) Ethylene (133 mg, 4.75 mmoles), identified by the aid of its IR-spectrum, was collected in the trap at -195° with traces of acetylene.

Ratio of 1:3 chromium(III)chloride and vinylmagnesium chloride

A solution (42 ml) of vinylmagnesium chloride (9.064 g, 0.105 mole) in tetrahydrofuran was added to a suspension of chromium trichloride tristetrahydrofuranate (13.04 g, 0.035 mole) in tetrahydrofuran (50 ml) at -78° . The Gilman test remained positive at this temperature; however, at some temperature between -60 and -50° the reaction went to completion (negative Gilman test). A color change to dark brown took place and the reaction mixture was allowed to warm up to room temperature. Volatile materials were collected in a trap cooled to -126° and after 2.5 h the gaseous mixture was brought into the vacuum apparatus and separated as described above. Thus the products ethylene (64 mg, 2.26 mmoles) and butadiene (105 mg, 1.95 mmoles) could be identified by means of their vapor pressures and infrared spectra.

The reaction mixture on hydrolysis with water yielded no benzene; however, a small amount of ethylene and butadiene resulted. A total residue of 2.35 g of an unidentified brown-yellow oil was obtained on removal of the solvents.

Deuterolysis of the reaction mixture, vinylmagnesium chloride and chromium(III) chloride (molar ratio 3:1)

The experiments involving 3 moles of vinylmagnesium chloride and 1 mole of chromium trichloride tristetrahydrofuranate in tetrahydrofuran were carried out similar to that described immediately above. Any gaseous material was collected, separated and investigated as mentioned before.

(a) *Deuterolysis at -60 and -50° .* The 3:1 mixture was deuterolyzed in one experiment at about -60° , in another at -50° . The IR spectra of the gaseous materials collected were recorded at 255 and 170 mm of mercury. In both cases, by comparison with an authentic sample*, the gaseous product was monodeuterated ethylene mixed with some ethylene.

Vinylmagnesium chloride (0.21 mole) and 0.07 mole of chromium(III) chloride tristetrahydrofuranate using 100 ml of tetrahydrofuran, yielded on deuterolysis at -50° with 8 ml deuterium oxide, 110 mg (3.8 mmoles) of deuterated ethylene. The amount of butadiene species was found to be 1-2% of the monodeuteroethylene.

(b) *Deuterolysis at 0° .* In another experiment the 3:1 mixture was warmed up to 0° and then treated with deuterium oxide. From the IR spectrum obtained, no absorption bands corresponding to a deuterated ethylene could be detected.

Vinylmagnesium chloride, chromium(III) chloride and diphenylacetylene in tetrahydrofuran (molar ratio 3:1:1)

Vinylmagnesium chloride (6.5 g, 0.075 mole) was added to chromium(III) chloride tristetrahydrofuranate (9.38 g, 0.025 mole) and 4.45 g (0.025 mole) of diphenylacetylene in 240 ml tetrahydrofuran at -75° . The reaction mixture was slowly warmed up to room temperature (3.5 h) and left standing overnight under nitrogen. After refluxing the dark solution for one hour the reaction mixture was cooled to room temperature and the solvent evaporated under vacuum. The residue was hydrolyzed with dilute hydrochloric acid and the product isolated with the aid of benzene. The dark brown oil (6.12 g) thus obtained was triturated with hexane. The insoluble

* Monodeuterated ethylene was prepared from the vinylmagnesium chloride solution and deuterium oxide at 0° . IR spectra of the gas at 385, 255 and 146 mm of mercury in a 5 cm cell were recorded for comparison.

material (0.68 g) yielded only hexaphenylbenzene (70 mg, m.p. and mixed m.p. 408–415°) isolated by chromatography on alumina (act. I), the remainder being intractable tars which were not further investigated. The hexane soluble material (5.43 g) was chromatographed on alumina (act. I) to give: (i) an unidentified colorless oil (0.614 g); (ii) diphenylacetylene (100 mg, 0.56 mmole), m.p. and mixed m.p. 60–61°; (iii) *trans*-stilbene (704 mg, 3.9 mmole), m.p. and mixed m.p. 123–125°; (iv) 1,2,3,4-tetraphenylbenzene (790 mg, 2.1 mmole), m.p. and mixed m.p. 194–195°, the IR spectrum of this material was superimposable with that of an authentic specimen⁹; (v) hexaphenylbenzene (150 mg, 0.28 mmole), m.p. and mixed m.p. 410–415°. The remainder was a series of unidentified, intractable tars and syrups.

Vinylmagnesium chloride, chromium(III) chloride and dimethylacetylene in tetrahydrofuran (molar ratio 3:1:3)

Vinylmagnesium chloride (0.099 mole) was added to chromium(III) trichloride tristetrahydrofuranate (5.55 g, 0.035 mole) and 8 ml (5.4 g, 0.1 mole) dimethylacetylene in 400 ml of tetrahydrofuran at –70°. After slowly warming the reaction mixture to room temperature (4 h), the dark solution after standing overnight (under nitrogen) was refluxed for one hour. The solvent was evaporated *in vacuo* and the residue was treated with 5% hydrochloric acid. The resulting mixture was extracted with ether which was washed with a bicarbonate solution and finally the ether was removed on the steam bath. The residue was distilled at 15 mm of mercury through a column to give the following fractions: (i) at ca. 80°, a yellow oil (515 mg, 3.85 mmoles) which was identified by vapor phase chromatography and IR spectrum with the aid of an authentic specimen 1,2,3,4-tetramethylbenzene; (ii) over 100°, hexamethylbenzene (4.1 g, 25.3 mmoles), m.p. and mixed m.p. 163–165°, was identified by comparison with an authentic specimen.

SUMMARY

The reaction of vinylmagnesium chloride with chromium trichloride tristetrahydrofuranate in tetrahydrofuran in various molecular ratios has been examined. When equimolar amounts of the reagents are used the chromium(III) species is reduced to chromium(II) with the concomitant formation of butadiene, ethylene and some acetylene. Deuterolysis of the 3:1 mixture at low temperatures furnishes mono-deuteroethylene indicating, in solution, the presence of a σ -bonded vinylchromium. With disubstituted acetylenes the vinylchromium system yields tetrasubstituted as well as the anticipated trimeric hexasubstituted benzene derivatives.

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