Präparative Vorschrift

Sämtliche Arbeiten müssen unter sorgfältig gereinigtem Stickstoff durchgeführt werden.

In einen 500-ml-Dreihalskolben mit N_2-Hahn, Tropftrichter, KPG-Rührer und Rückflusskühler mit Hg-Rückschlagventil gibt man 6 g (37 mMol) wasserfreies $FeCl_3$ und kühlt auf —50° ab. Durch den Tropftrichter lässt man eine auf —50° gekühlte Lösung von 15 ml Cycloheptatrien und 15 ml Cycloheptadien-(1.3) in 120 ml absolutem Äther einlaufen. Nun wird eine Grignardlösung, bereitet aus 7 g (288 mMol) Mg und 31 ml Isopropylbromid in 100 ml Äther, im Zeitraum von 10 min zugetropft. Man lässt den Kolben sich auf Raumtemperatur erwärmen und bestrahlt 8 Std. mit dem UV-Licht einer Quecksilber-Hochdrucklampe, die in etwa 2 cm Entfernung von der Kolbenwandung angebracht ist. Die auftretende Gasentwicklung ist nach Ablauf dieser Zeit weitgehend zum Stillstand gekommen.

Die Hydrolyse wird in einem 1-l-Dreihalskolben mit einem Gemisch von 100 ml Methanol und 100 ml Äther, in das man die rotbraune Reaktionslösung bei —50° unter heftigem Rühren langsam eintropfen lässt, durchgeführt. Nach Absaugen des Hydrolysegemisches über eine mit Glaswolle überschichtete G3-Fritte werden zuerst Äther und überschüssiges Methanol im Wasserstrahlvakuum, anschliessend die überschüssigen Olefine im Hochvakuum unter gelindem Erwärmen mit einem Fön möglichst vollständig entfernt. Aus dem verbleibenden Rückstand löst man den Komplex mit etwa 150 ml Hexan heraus und engt die rotbraune Lösung nach Filtration über eine etwa 10 cm hohe Schicht von Al_2O_3 auf wenige ml ein. Dann wird über eine 1 m lange Säule an Al_2O_3 "Woelm" (4 % H_2O) mit Hexan als Eluierungsmittel chromatographiert. Die ersten ml des Eluates werden verworfen, aus dem übrigen Teil scheiden sich nach Einengen bei —78° C die gesuchten Kristalle aus. Sie werden zur Reinigung nochmals aus Hexan unter Tiefkühlung umkristallisiert.

Ausbeute: 2.8 g entspr. 31 % bez. auf $FeCl_3$. (Gef.: C, 69.45; H, 7.71; Fe, 22.82 %; Mol.-Gew. kryoskop. in Benzol, 248. $C_{14}H_{18}Fe$ ber.: C, 69.44; H, 7.40; Fe 23.07 %; Mol.-Gew., 242.13.)

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Studies on an iron-σ-propargyl complex

Recent studies on the protonation of metal–σ-allyl complexes[1] and iron–1-cyanoalkyl complexes[2] show that a proton is added to the 3-carbon and that ethylenic or ketenimine–metal complexes respectively are formed. We have prepared the propargyl complex $C_5H_5Fe(CO)_2CH_2C{\equiv}CH$ (I) and studied its protonation reaction with a view to obtaining a metal–allene complex.

The propargyl complex (I) may be prepared in small yield by the reaction of the sodium salt[3] $Na^+[C_5H_5Fe(CO)_2]^-$ with propargyl bromide. The complex (I) forms deep yellow crystals which are only slowly decomposed in air. It is readily soluble in light petroleum and other common organic solvents; the solutions are stable when kept under nitrogen but are readily oxidised on exposure to air. The complex (I) is also slightly soluble in water and appreciably soluble in concentrated hydrochloric acid, with which it reacts. It is not possible to recover the complex (I) from the acid solutions by neutralisation followed by re-extraction with ether. It may be noted that in contrast the iron-1-cyanoalkyl complexes are reversibly protonated by aqueous mineral acids[2]. The infrared and proton magnetic resonance spectra of the complex (I) are given in the experimental section together with some assignments. The spectra are entirely consistent with the formulation of the complex (I) given above and this evidence is not further discussed.

Reaction of the propargyl complex (I) *with acids*

Treatment of light petroleum solutions of the complex (I) with dry hydrogen chloride results in the immediate formation of a deep yellow precipitate. Passing the hydrogen chloride for a further 5 min changes the precipitate to deep red crystals which were identified as the chloro complex $C_5H_5Fe(CO)_2Cl$[3]. The formation of the chloro complex indicates that the reaction of the complex (I) with excess hydrogen chloride does not destroy the $C_5H_5Fe(CO)_2$ system in the molecule. Attempts to protonate the complex (I) with anhydrous perchloride acid in benzene, or fluoroboric acid in ether resulted either in decomposition of the complex or the formation of intractable oils respectively. It was, however, found possible to isolate the hexachloroantimonate of the cation formed by the protonation of complex (I) in concentrated hydrochloric acid. The fawn hexachloroantimonate of the cation formed from complex (I) may be recrystallised, with slight decomposition, from liquid sulphur dioxide. Analyses and spectra show that the cation hexachloroantimonate readily decomposed in solution, even in liquid sulphur dioxide, and, despite very rapid recrystallisations, it was not found possible to obtain consistent analyses. However, the average of four carbon analyses are within 1.5 % for the compound $[C_5H_5Fe(CO)_2C_3H_4]^+SbCl_6^-$ which would be expected if the complex (I) undergoes the expected protonation reaction. The infrared spectrum of the cation hexachloroantimonate given in the experimental section, is consistent with a formulation $[C_5H_5Fe(CO)_2L]^+SbCl_6^-$, where L is a hydrocarbon ligand. Due to decomposition in liquid sulphur dioxide, the complete proton magnetic resonance spectrum of the cation could not be obtained. However, a band at 4.02 τ, assignable to the protons of a C_5H_5-metal system, could be identified and appears 1.08 τ lower than in the neutral complex, which is consistent with a higher oxidation state of the metal in the cation.

Hydrolysis of a dimethylsulphoxide solution of the cation hexachloroantimonate with water gave acetone as the most volatile product which was identified from the infrared spectrum.

Discussion

The above evidence shows that the propargyl complex (I) is readily and irreversibly protonated by hydrochloric acid and that the $C_5H_5Fe(CO)_2$ system is not thereby destroyed. Acetone is the product of hydrolysis of allene under acid conditions.

Therefore, the formation of acetone on hydrolysis of the cation hexachloroantimonate is evidence that there may be an allene system in the cation. The π-allene cation $[C_5H_5Fe(CO)_2\text{-}\pi\text{-}CH_2{=}C{=}CH_2]^+$ would be expected if the course of the protonation of the propargyl complex (I) is similar to that of the isoelectronic iron–1-cyanoalkyl complexes.

Experimental

Microanalyses were carried out in the Microanalytical Laboratory, Lensfield Road, Cambridge. Preparations, reactions, and purification procedures were carried out under nitrogen or in a vacuum. Light petroleum is AnalaR material, b.p. 30–40°.

Dicarbonylpropargylcyclopentadienyliron

Tetracarbonyldicyclopentadienyldiiron[3] (10 g) in tetrahydrofuran (75 ml) was stirred with an excess of 3% amalgam for 1 h. The resulting solution of the sodium salt $Na^+[C_5H_5Fe(CO)_2]^-$ was slowly added to an excess (15 ml) of propargyl bromide in tetrahydrofuran which was cooled in a dry ice–acetone bath. The mixture was stirred, allowed to warm up to room temperature and was stirred for a further 1 h. The solvent and excess of propargyl bromide were removed under vacuum and the residue was extracted with 1:1 ether–light petroleum. The extract was concentrated and the chromatographed on an almina column made up in light petroleum, eluting with 1:1 ether–light petroleum. The deep orange band which came after the red-brown band of the other main product, namely, the binuclear complex $[C_5H_5Fe(CO)_2]_2$ was collected. The eluate was concentrated, re-chromatographed as before, and the solvent removed from the second eluate giving a solid orange residue which was recrystallised from light petroleum affording deep orange-yellow crystals. M.p. 96–96.5°. Yield ca. 15%. (Found: C, 55.7; H, 3.8; Fe, 26.1; mol.wt., cryoscopic in dioxane, 215. $C_{10}H_8O_2Fe$ calcd.: C, 55.6; H, 3.7; Fe, 25.9%; mol.wt., 216.) Also separated from the reaction mixture by chromatography was a very small amount of petrol soluble compound which the infrared spectrum showed to contain carbonyl groups. This product was not further investigated.

Reaction of dicarbonylpropargylcyclopentadienyliron with acid. A. Dicarbonylpropargylcyclopentadienyliron (0.5 g) in light petroleum (50 ml) was treated with anhydrous hydrogen chloride. Immediately a fawn precipitate appeared and when all the colour had gone from the light petroleum (1 min) the addition of the hydrogen chloride was stopped, further passage of hydrogen chloride for 5 min changes the precipitate to a deep red crystalline $C_5H_5Fe(CO)_2Cl$. The light petroleum was decanted from the solution, the precipitate was washed with light petroleum and dried under vacuum. This procedure affords the crude cation chloride which could not be further purified. The cation chloride was dissolved in water (3 ml) and immediately a solution of hexachloroantimonic acid was added. The cation hexachloroantimonate, precipitated as a brown solid which was recrystallised from liquid sulphur dioxide–ether. Yield 60% Traces of decomposition products were evident despite repeated recrystallisations. [Found: (average of 4 analyses) C, 20.4; H, 1.3. $C_{10}H_9O_2FeSbCl_6$ calcd.: C, 21.8; H, 1.7%.]

B. Improved yields of the hexachloroantimonate were obtained by shaking a solution of the propargyl complex (I) in light petroleum with hexachloroantimonic acid in concentrated hydrochloric acid (5 ml) and filtering the solution immediately.