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A ONE-STEP SYNTHESIS OF BIS(h^5-CYCLOPENTADIENYL)ZIRCONACYCLOPENTADIENE COMPOUNDS

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Summary

Bis(h^5-cyclopentadienyl)zirconacyclopentadiene complexes were prepared by reduction of zirconocene dichloride in THF with magnesium in the presence of various alkynes. Hydrolysis leads to the corresponding (*E*,*E*)-butadiene derivatives.

Introduction

Metallacyclic derivatives of transition metals have been extensively investigated in recent years [1,2] since they are believed to serve as key intermediates in various homogeneous catalytic processes. Our interest in the polymerization of alkynes by zirconocene dichloride/ethylaluminum dichloride [3,4] prompted us to seek more facile and productive methods of synthesis of bis(h^5-cyclopentadienyl)zirconacyclopentadienes. Existing synthetic methods are either limited to activated alkynes [5—8] or are lengthy, resulting in relatively low net yields [9]. The method is based on that for the production of $Cp_2Ti(CO)_2$ from Cp_2TiCl_2 [10].

Experimental

Starting materials and solvents. Zirconocene dichloride was purchased from Aldrich Chemical Co. and used as received. The alkynes 2-butyne, 3-hexyne and diphenylacetylene were obtained from Farchan Division and used without further purification.

Tetrahydrofuran and diethyl ether were dried over sodium and distilled before use from sodium/benzophenone under nitrogen. In order to achieve good yields, it is essential that the solvents be dry and oxygen free.

Physical methods. NMR spectra were taken on a Varian EM 360 spectrometer using TMS as an internal standard. ^{13}C spectra were recorded on a Varian FT80-

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A multinuclear NMR spectrometer. Mass spectra were sampled on a Finnigan 1015 mass spectrometer.

Preparation of the complexes. All operations were carried out under nitrogen using standard Schlenk tube techniques or in a nitrogen-filled glove box. Since the preparations of the various complexes are essentially identical, only the synthesis of the tetraphenyl derivative is given in detail.

Synthesis of bis(h^5-cyclopentadienyl)-2,3,4,5-tetraphenylzirconacyclopentadiene

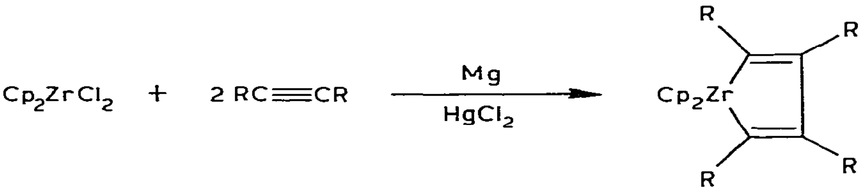
To a 250 ml, 3-necked flask [11] equipped with a nitrogen inlet, a rubber septum, and a nitrogen outlet connected to an oil bubbler, was added 2.91 g (0.01 mol) of zirconocene dichloride, 1.2 g (0.05 mol) of Mg powder, 2.71 g (0.01 mol) of $HgCl_2$, and 7.12 g (0.04 mol) of diphenylacetylene. The flask was flushed with N_2 for 30 min, and then 50 ml of freshly distilled THF was added by means of a syringe through the septum. The flow of N_2 was halted and the reaction mixture was magnetically stirred at room temperature. Within minutes the reaction mixture darkened. The stirring was maintained until a proton NMR spectrum showed only one π-cyclopentadienyl-containing compound was present (about 10 h). The solvent was removed under vacuum (10^{-2} Torr) at room temperature and the flask was transferred to a nitrogen-filled glove box. The dark red-brown solid was washed several times with ether to remove unreacted diphenylacetylene, dissolved in a minimum amount of benzene and filtered. The solvent was removed under vacuum and the residue was recrystallized from methylene chloride/pentane giving 4.9 g (85%) of the product.

Synthesis of the other zirconacyclopentadienes

The tetraethyl derivative was prepared in a manner similar to that described above, except that the reaction time was 6 h. After purification, the compound was obtained in 80% yield. The tetramethyl derivative required 8 h reaction time and was obtained in 85% yield. Since 2-butyne has a low boiling point, the alkyne was added just before the flow of N_2 was stopped and the reaction was allowed to proceed in a closed system. All connections were secured with rubber bands.

Results and discussion

The general reaction carried out in this work is shown in the equation.

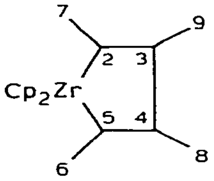


(R = C_6H_5 , C_2H_5 , CH_3)

The tetraphenyl derivative is a known compound, [12], and infrared and NMR spectral properties, as well as melting point, of the compound prepared in this work and the authentic compound are identical [13]. The compound was dissolved in $CHCl_3$ and treated with aqueous HCl solution in a manner similar to that reported by Freedman [14]. Obtained in quantitative yield was (*E*, *E*)-1,2,3,4-tetraphenylbutadiene (m.p. 183° C).

The tetraethyl derivative has also been reported, and the compound prepared in this work and the authentic compound [15] are identical in color, spectral properties, and melting point. The proton NMR spectrum shows signals at δ 6.07 (s, 10H), 2.4 (q, 4H), 2.27 (q, 4H), 1.05 (t, 6H) and 0.96 (t, 6H). The hydrolysis product, (*E*,*E*)-4,5-diethyl-3,5-octadiene [13] shows a proton NMR spectrum as follows: δ 5.3 (t, 2H), 2.1 (overlapping quartets 8H), 0.95 (t, 6H) and 0.90 (t, 6H).

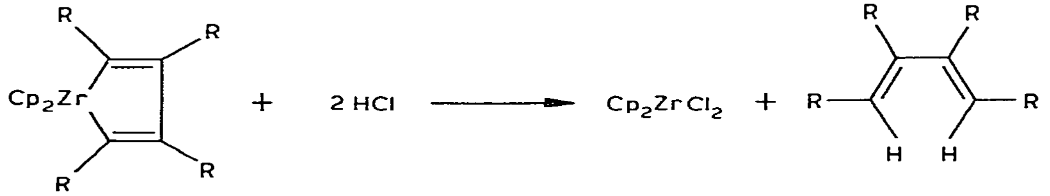
The new compound prepared in this work, bis(h^5-cyclopentadienyl)-2,3,4,5-tetramethylzirconacyclopentadiene, was characterized by spectral properties: mass, parent *m/e* 329; ^1H NMR, δ 6.05 (s, 10H), 1.93 (s, 6H), 1.80 (s, 6H); ^{13}C NMR, δ 181.92 (C 2,5), 132.91 (C 3,4), 109.71 (Cp carbons), 20.02 (C 6,7), 14.6 (C 8,9). Off-resonance decoupled ^{13}C spectra showed that the signal at δ 109.7 splits into a doublet, and the peaks at δ 20.02 and 14.6 split into quartets. The carbon atoms are numbered as shown below. Anal. Found: C, 64.85; H, 6.68. $C_{18}H_{22}Zr$ calcd.: C, 65.65; H, 6.69%.



The hydrolysis product is (*E*,*E*)-3,4-dimethyl-2,4-hexadiene [16], a liquid with b.p. 134° C at 740 Torr, and ^1H NMR signals at δ 5.6 (q, 2H), 1.77 (s, 6H), and 1.70 (d, 6H).

The synthesis reported herein appears to be general. We have prepared several other zirconacyclopentadiene derivatives and also a zirconacyclopentane molecule from reaction with alkenes. In all cases, the compounds are prepared in greater than 80% yield.

The practical aspect of this research is the hydrolysis reaction of the compounds to yield exclusively the corresponding (*E*,*E*)-butadiene compounds. The reaction is quantitative, and this constitutes a convenient, stoichiometric synthesis of substituted butadiene molecules of specific configuration:



Thus, the starting material, zirconocene dichloride, may be recovered in the preparation of the butadiene derivatives.

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