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Oligomerization of alkynes by hafnocene dichloride/ethylaluminum dichloride

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Summary

The $Cp_2HfCl_2/C_2H_5AlCl_2$ system ($Cp = \eta^5$-cyclopentadienyl) was found to be an active homogeneous catalyst for the oligomerization of both terminal and internal alkynes. Apparently, the mechanism of oligomerization occurs by successive insertion of the alkyne into the hafnium-carbon bond of a cationic intermediate, as evidenced by the interception of the highly substituted, sterically bulky, 1-trimethylsilyl-1-propyne.

Introduction

Much effort in our laboratory has been extended toward the elucidation of the role of transition metal complexes in promoting polymerization of alkynes. Our more recent studies have been on the Group IV metallocenes, Cp_2TiCl_2 and $Cp_2ZrCl_2/C_2H_5AlCl_2$, and also on the metallacyclopentadienes made from these complexes (1,2,3). In general, the titana- and zirconacyclopentadienes were found to promote oligomerization of acetylenes by an insertion process to expand the metallacycles, elimination of which resulted in the formation of a polyalkyne.

It was of interest, therefore, to investigate the $Cp_2HfCl_2/C_2H_5AlCl_2$ system with regard to its catalytic properties toward alkynes and attempt to elucidate the mechanism of this homogeneous system in reactions toward alkynes.

Experimental

Solvents and starting materials. Methylene chloride (Fisher) was refluxed over P_2O_5 and distilled under nitrogen before use. Ether and toluene were purified by refluxing over Na/benzophenone and distilled under nitrogen. Alkynes were distilled under vacuum. Styrene was stirred over CaH_2 for two days under nitrogen and distilled under vacuum. Isobutylene (99.0%, Linde) was dried by passing the gas through a 4 ft column packed with 3A molecular sieves and barium oxide, and condensed inside a dry box. Ethylaluminum dichloride (neat and 1.0M in hexane, Aldrich) was used as received as was hafnocene dichloride.

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Physical methods. Infrared (IR) spectra were recorded on a Perkin-Elmer 597 grating spectrophotometer. ^1H NMR spectra were obtained on a Varian EM360 spectrometer using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. A Varian XL-300 spectrometer served as a source of high-resolution spectra. Mass spectra were taken on a Finnigan 1015 S/L mass spectrometer.

Molecular weights of the polyalkynes were determined by Schwartzkopf Laboratory, Woodside, NY. The molecular weights of polystyrene and polyisobutylene were determined by gel permeation chromatography (Waters Associates 6000 A pump, UV and RI dual detectors, microstyrogel columns of 10^6, 10^5, 10^4, 10^3, 500, 100 Å).

Oligomerization procedure. The experimental procedures for the oligomerization of all alkynes are analogous; therefore, only one of these is described in detail.

Oligomerization of phenylacetylene. Into a 250 ml, 2-necked flask fitted with an argon inlet and a rubber septum was added 0.759 g (2 mmol) of hafnocene dichloride. The flask was flushed with argon for 30 min, and 25 ml of CH_2Cl_2 was injected through the septum followed by 2 ml (2 mmol) of ethylaluminum dichloride in hexane. The solution became homogeneous instantly and acquired a pale yellow color. After 45 min. the flask was cooled to -78 °C and 4.0 g (40 mmol) of phenylacetylene was injected dropwise over a period of 10 min. The reaction was allowed to proceed for 1 h, and 10 ml of chilled methanol was added to deactivate the catalyst. The reddish-brown compound that precipitated from solution was collected by filtration, dissolved in a minimum amount of CCl_4, and subjected to column chromatography on neutral alumina. Elution with 1:3(V/V) CCl_4/hexane brought down the first band which upon evaporation of the solvent yielded a yellow solid. A second band was eluted with 1:1 (V/V) CCl_4/ether and gave a yellow-red solid (combined yield = 3.1 g, 77.5%). The products were purified further by repeated recrystallization from CCl_4/CH_3OH. Both products exhibited identical spectroscopic properties and were identified as polyphenylacetylene by their IR and NMR spectra and their molecular weights.

Oligomerization of the alkynes. The monomers 1-hexyne and 1-phenyl-1-propyne were also induced to oligomerize by methods analogous to those described above for phenylacetylene. Detalis are presented in Table 1.

Polymerization of styrene. Styrene was induced to polymerize by methods analogous to those described above. In this case, 3.12 g of styrene was used and the reaction temperature was -60 °C. The resulting white polymer was collected by filtration, dissolved in THF, and passed through a silicon gel column several times. The THF solution containing polystyrene was washed with sodium potassium tartrate solution and then with distilled water to remove any remaining aluminum residues. The polymer was then subjected to the cycle of dissolution in THF and precipitation with methanol. The dried polymer indicated a 100% conversion of the monomer.

The polymerization of isobutylene was also carried out in a manner analogous to that described for styrene.

Reaction of 1-trimethylsilyl-1-propyne with $Cp_2HfCl_2/C_2H_5AlCl_2$. To a 250 ml, 2-necked flask fitted with an argon inlet and rubber septum and containing 3.02 g (8 mmol) of hafnocene dichloride under argon, was added 25 ml of methylene chloride and 1.01 g (8 mmol) of neat ethylaluminum dichloride. After the catalyst aged for 45 min, 0.848 g (8 mmol) of 1-trimethylsilyl-1-propyne was added and the reaction mixture was stirred for 96 hr at room temperature. The reaction mixture was then cooled to 0°C and 3.23 g (32 mmol) of triethylamine was added followed by 0.8 ml of water. The reaction mixture was diluted with 50 ml of methylene chloride; the resulting red-brown solution was washed with water, 5% HCl, and a saturated solution of sodium bicarbonate, and dried over anhydrous sodium sulfate. The solvent was removed and the residue was taken up in methylene chloride and passed through a short silica gel column. The resulting product (0.42 g, 37.5% yield) was analyzed by GC-MS; that study indicated that two products were present, one of m/e 204.5 and one at m/e 176.5. A parallel control reaction duplicating the conditions employed above was carried out, except that hafnocene dichloride was absent.

Table I

Monomers Oligomerized by $Cp_2HfCl_2/C_2H_5AlCl_2$

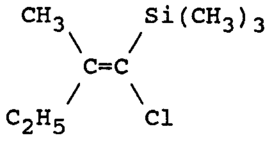
Monomer	Conditions	Conversion Percent	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$
$C_6H_5C\equiv CH$	CH_2Cl_2, -78°C	77.5	700	-
$C_6H_5C\equiv CH$	Toluene, -78°C	69.0	500	-
$C_4H_9C\equiv CH$	Toluene, RT	91.6	600	-
$C_6H_5C\equiv CCH_3$	Toluene, 70°C, 6 hr	21.5	700	-
Isobutylene	CH_2Cl_2, -78°C	100	245,000	1.77
Styrene	CH_2Cl_2, -60°C	100	37,000	3.15
Styrene	Toluene, -60°C	100	4,000	4.86

Results and Discussion

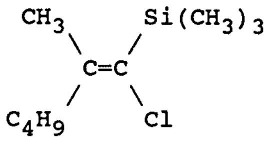
Like the $Cp_2ZrCl_2/C_2H_5AlCl_2$ catalyst system, the hafnium system produced linear, polyconjugated polymers, exclusively. The IR and NMR spectra of polyphenylacetylene indicate that the double bonds in the polyconjugated structure are mainly *trans*. This comes from an investigation of the 915 and 890 cm^{-1} band intensities in the IR spectrum of the polymer, in which the 915 cm^{-1} band is clearly the predominant one(4). The spectral properties of the other polyalkynes compare favorably with those reported elsewhere for the same polymers(5,6). The polyolefins prepared in this work are similar in ^{1}H NMR spectral and Tg studies (110°C and -60°C) reported earlier by other workers(7,8).

In the proton NMR spectrum of polyphenylacetylene, a broad olefinic proton signal appears to overlap the aromatic absorption. The deshielding of the olefinic proton is attributed to the conjugation of the polymer backbone with the aromatic rings pendant to the chain. Furthermore, the first fraction of the polymer obtained after chromatographic purification shows the presence of an ethyl group in the ^{1}H NMR spectrum (δ2.35, 2H, q; δ0.8, 3H, t). The ethyl group most likely arises from the initiation step, where the initiating species is believed to be $Cp_2HfC_2H_5^+AlCl_4^-$.

Mechanism. The reaction of the catalyst system with 1-trimethylsilyl-1-propyne, a sterically bulky, alkynyl substrate, which would limit alkyne insertion largely to the initial step, was carried out with the expectation that isolation of the first formed product could provide insight into the mechanism of oligomerization. Two products were separated and identified by a gas chromatographic-mass spectrometric studies:

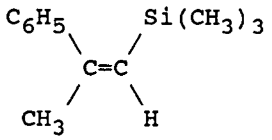


(a)



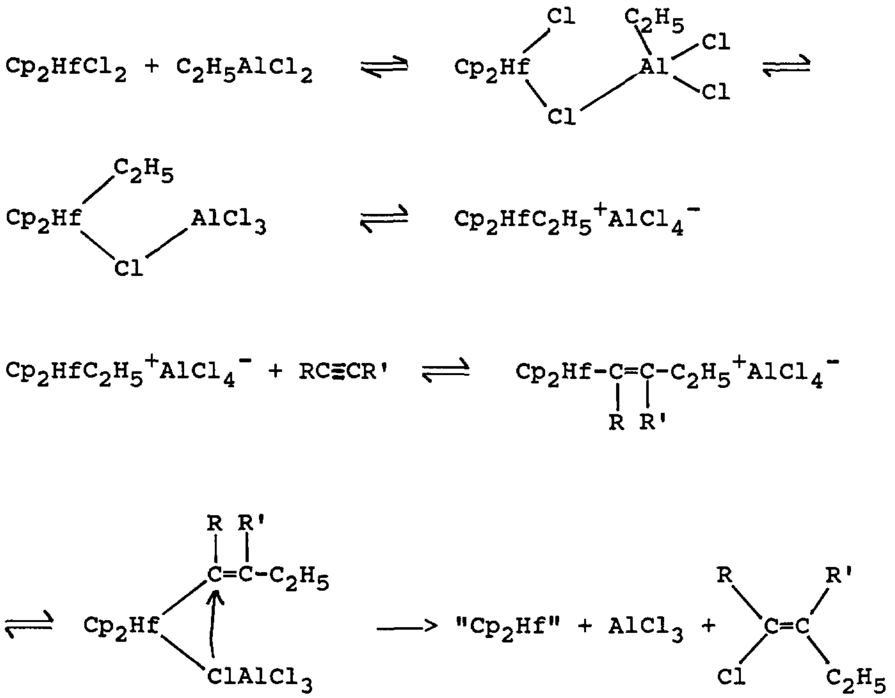
(b)

Recently, Eisch et al. studied the interaction of equimolar amounts of the titanocene dichloride/methylaluminum dichloride catalyst system with $C_6H_5C{\equiv}CSi(CH_3)_3$, and intercepted the initial insertion product(9). The compound isolated, after hydrolysis, was



which led to the conclusion that the initiating species for polymerization of olefins is $Cp_2TiCH_3^+AlCl_4^-$, and propagation occurs by insertion of the olefin into the Ti-C bond. Jordon, et al., have studied the dimethylzirconocene catalyst and confirmed the initiating species for polymerization of olefins as $Cp_2ZrCH_3(THF)^+BPh_4$(10).

Oligomerization of alkynes by the $Cp_2HfCl_2/C_2H_5AlCl_2$ system appears to be analogous to the titanocene and zirconocene systems above. In the reaction of the catalyst with $CH_3C{\equiv}CSi(CH_3)_3$, the products (a) and (b) can be explained as arising in the following manner.



In the case of product (b), where a butyl group has taken the place of the ethyl ligand in (a), the C_4 fragment can arise from prior insertion of ethylene into the $Hf-C_2H_5$ bond. Ethylene is generated in small amounts from $C_2H_5AlCl_2$(10).

Further evidence that propagation proceeds by an insertion of the alkyne into a Hf-C bond comes from polymerization studies of styrene with the same catalyst system. There is a significantly higher molecular weight obtained when methylene chloride is used as the solvent ($\overline{Mn}$ = 37,000) than when toluene is used ($\overline{Mn}$ = 4,000), showing the polar nature of the initiator. Complete inhibition of polymerization of styrene and isobutylene was observed in the presence of such Lewis bases as ether and also where the monomer dimethylacetylene dicarboxylate was used, showing that coordination of such bases blocks the coordination site of the monomer and prevents insertion.

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