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LINEAR POLYMERIZATION OF PHENYLACETYLENE USING SOME (TRIPHENYLPHOSPHINE)PLATINUM COMPLEXES

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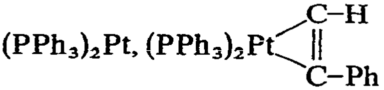
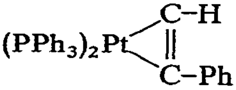
SUMMARY

The polymerization of phenylacetylene in the presence of *cis*- and *trans*-$(PPh_3)_2PtCl_2$, *trans*-$(PPh_3)_2PtHCl$, $(PPh_3)_2Pt$,  $(PPh_3)_2Pt\begin{matrix}C-H\\ \|\\ C-Ph\end{matrix}$ and *cis*- and *trans*-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ has been studied at room temperature and at high temperature. In the first case complexes with the acetylide radical σ-bonded to the Pt atom were isolated, and are thought to be the initial intermediates in the linear polymerization of phenylacetylene which occurs at high temperature. A mechanism for the polymerization reaction is proposed.

INTRODUCTION

In recent years there has been increasing interest in the catalytic activity of transition metal complexes in aromatization or polymerization of acetylenic hydrocarbons[1,2]. In the many experiments in this connection, the active intermediate complexes have seldom been isolated in the first stages of the polymerization reaction, and thus hypotheses on reaction mechanisms are based on indirect experimental evidence.

In the case of $(PPh_3)_2Ni(CO)_2$, Meriwether and coworkers[3] assumed that the active polymerization catalyst was a nickel–phosphine–acetylene complex, similar to the platinum–phosphine–acetylene complex



$$(PPh_3)_2Pt\begin{matrix}C-H\\ \|\\ C-Ph\end{matrix}$$

(I)

prepared by Chatt[4] in 1957. According to Meriwether, the active complex is in equilibrium with an hydridic acetylide $(PPh_3)_2Ni(H)C{\equiv}CPh$, which could be responsible for both linear and cyclic polymerization. To test the Meriwether hypothesis we used as the catalyst in the polymerization reaction of phenylacetylene, the complex (I) and also some other bis(triphenylphosphine) complexes of Pt, namely *cis*-$(PPh_3)_2PtCl_2$ (II) and *trans*-$(PPh_3)_2PtCl_2$ (III) (refs. 5 and 6), *trans*-$(PPh_3)_2PtHCl$ (IV) (ref. 7), $(PPh_3)_2Pt$ (V) (ref. 8), *cis*-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ (VI) and *trans*-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ (VII); (VI) and (VII) are new compounds. The method of preparation and their properties are described in the preceding paper[18].

Bulk polymerizations have been carried out at various temperatures. No solvent was used, in order to avoid a possible inactivation of the catalyst due to competitive coordination of the solvent molecules to the active complex.

RESULTS

Reactions of bis(triphenylphosphine)platinum complexes with phenylacetylene at room temperature

(I), (II), (III), (IV), (V), (VI) and (VII) interact with phenylacetylene at room temperature, but no appreciable polymerization occurs. The course of the reaction was followed by taking aliquots of the mixture periodically and chromatographing then on silica gel columns using C_6H_6 and $C_6H_6/CHCl_3$ (1/1) as eluents. The separated products were identified by means of their UV spectra.

Bis(triphenylphosphine)platinum complexes (I), (II), (III), (IV) and (V) give *trans*-bis(triphenylphosphine)bis(phenylethynyl)platinum (VII) as the major product and the *cis* isomer (VI) in smaller amounts. The chloro complexes (II), (III), and (IV) give bis(triphenylphosphine)(phenylethynyl)platinum chloride (VIII).

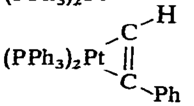
Trans-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ (VII) isomerizes slowly to the *cis* form (VI) in phenylacetylene at room temperature and an equilibrium stage is reached after several hours. It is evident from these results that σ-bonded acetylide species are always formed.

Reactions of bis(triphenylphosphine)platinum complexes with phenylacetylene at high temperature

When the reaction mixtures of (I), (II), (III), (IV), (V), (VI), and (VII) and phenylacetylene are warmed, polymerization occurs. Polymerization is almost complete in five or six hours if the reaction mixture is boiled. At 130° the reaction requires longer for completion, and an induction period is observed before the onset

TABLE 1

POLYMERIZATION REACTION OF PHENYLACETYLENE IN THE PRESENCE OF (TRIPHENYLPHOSPHINE)PLATINUM COMPLEXES

Complex	(mg)	Monomer (ml)	Moles of monomer / Moles of catalyst	Temp. (°C)	Reaction time (h)
cis-$(PPh_3)_2PtCl_2$	450	10	1600	Reflux	5
	395	8		130	48
trans-$(PPh_3)_2PtCl_2$	189	4.2	1725	130	48
trans-$(PPh_3)_2PtHCl$	360	10	1918	130	40
	360	10	1918	Reflux	5
$(PPh_3)_2Pt$	174.5	4.3	1615	130	40
	467	10	1605	Reflux	5
trans-$(PPh_3)_2(C{\equiv}CPh)_2$	93.5	8	7200	Reflux	4
	460.6	8	1415	130	48
cis-$(PPh_3)_2Pt(C{\equiv}CPh)_2$	93.5	7.2	6430	130	48

of the polymerization. Unreacted phenylacetylene and cyclic trimers (1,2,4- and 1,3,5-triphenylbenzene) were determined periodically using gas-chromatographic analysis of aliquots of the reaction mixture. The results are summarized in Table 1.

Conversion of phenylacetylene into linear polymers is virtually specific with all the catalysts used since only small amounts of cyclic trimers are found. At the end of the reaction a viscous mass is obtained, which dissolves easily in benzene. Polymers are then precipitated as yellow to brown powders by treatment with CH_3OH, CH_3COOH or n-hexane. For all the catalysts used the average molecular weight of the first polymer fraction is about 600. After several treatments with n-hexane the average molecular weight increases to 1400–1600. Polymers of phenylacetylene of similar molecular weight were obtained by thermal or catalytic polymerization[9-11].

The color of the various poly(phenylacetylene) fractions changes from yellow to red-brown. However, visible spectra are not characteristic, since polymers exhibit a continuous absorption in the visible region with an inflection at 340 mμ (refs. 9 and 12) and a maximum at 245 mμ. X-ray powder spectra of the polymers revealed a partial degree of crystallinity. From the lower fractions a linear dimer, probably 1,4-diphenylbutenyne is obtained by chromatography on silica gel columns using petroleum ether/benzene (8/2) as eluent.

IR spectra of various polymer fractions exhibit the usual bands of the aromatic monosubstituted ring, but they differ sometimes in the 800–1000 cm^{-1} region. A band at 970 cm^{-1}, which can be assigned to the out of plane C–H bending vibrations of the *trans*-R–CH=CH–R′ group, is sometimes more intense than a band at 890 cm^{-1}, which can be assigned to the C–H out of plane bending vibrations of the RR′C=CH_2 group. These two bands may possibly be related to two different terminations of the polymeric chains, or alternatively, the band at 890 cm^{-1} may be related to a different content of *cis* and *trans* units in the polymeric chain, as proposed recently by Kern[13].

Furthermore the double bond band at about 1650 cm^{-1} is very weak in some fractions and more intense in other ones. Absence of this band was related to a high

Complexes identified during the reaction	Phenyl acetylene unreacted (%)	Products, yields (%)		
		Trimers, 1,2,4- and 1,3,5,-triphenylbenzene	Linear polymers	Mol.wt. of initial polymer
(VII), (VIII)	22.0	5.6	72.4	610
(VII), (VIII)	8.8	3.3	87.9	580
(VII), (VIII)	22.0	0.46	77.5	610
(VII), (VIII)	2.45	7	90.5	580
	2.5	6.2	91.3	580
(VI), (VII)	Traces	1.8	98.2	820
	Traces	5.8	94.2	550
	Traces	1.1	98.9	510
(VI)	Traces	Traces	100	480
(VII)	Traces	Traces	100	590

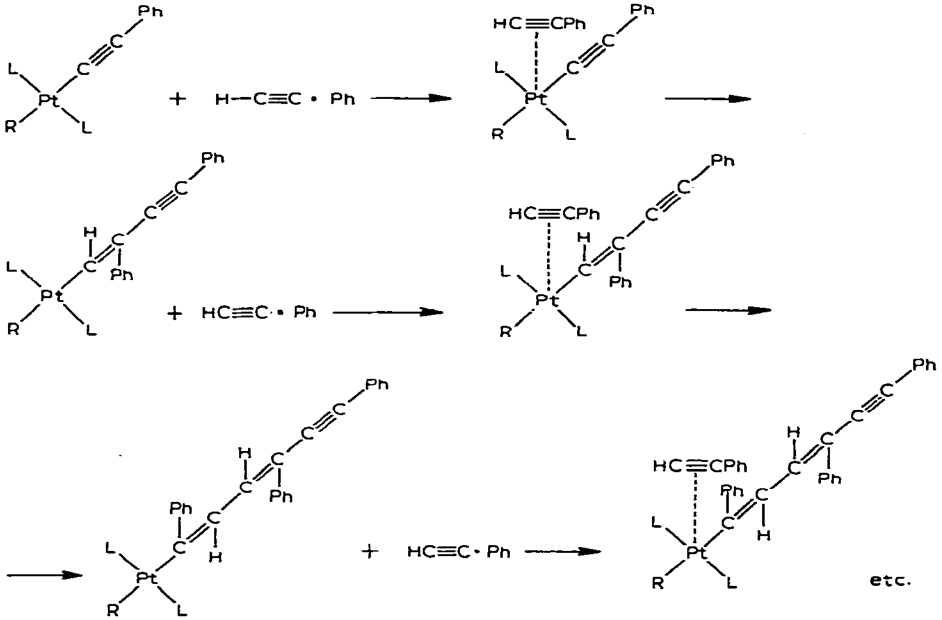
symmetry of the molecule of poly(phenylacetylene)[9,14–16] arising from a symmetrical *trans* configuration of phenyl rings along the chain.

More detailed studies on the structure of the polymers are in progress.

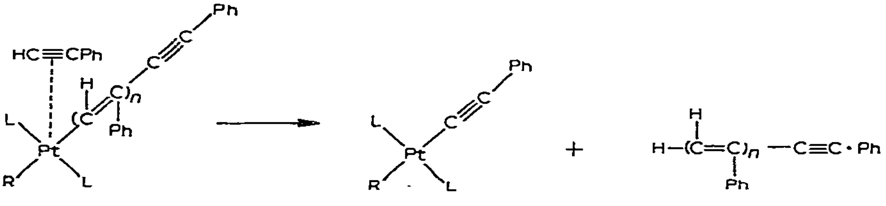
DISCUSSION

This is the first example of the catalysis of linear polymerization of phenylacetylene using Pt complexes. The intrinsic stability of platinum acetylides allowed identification of the active species, $(PPh_3)_2Pt(C{\equiv}CPh)Cl$ (VIII) and *cis*- and *trans*-$(PPh_3)_2Pt(C{\equiv}CPh)_2$ (VI, VII), in which the first molecule of the monomer is σ-bonded to the Pt atom. Formation of (VI), (VII), and (VIII) as active complexes is proof that an hydridic complex is not necessary to promote the polymerization reaction.

Coordination of another molecule of phenylacetylene to the active complex is probably the second step of the polymerization ($L = PPh_3$; $R = C{\equiv}C{-}Ph$ or Cl):



The polymer chain begins by insertion of a π-coordinated molecule of the monomer in the ethynyl–platinum bond. The growth of the chain is interrupted when the π-bonded monomer transfers its acidic hydrogen to the growing chain, regenerating the starting complex (A) as follows:



(B) (A)

The rate determining step is probably the formation of the penta-coordinated complex (B).

The complex (VII) is the major product in all reactions carried out at room temperature. It seems possible that it is also the most active catalyst but we do not have sufficient experimental evidence to rule out catalytic activity in the corresponding *cis* (VI) or chloro (VIII) compounds.

EXPERIMENTAL

Molecular weights were determined by a Mechrolab Osmometer in $CHCl_3$. IR spectra were measured with a Perkin–Elmer model 800 spectrophotometer using nujol mulls. UV spectra were taken on both Beckman DK1 and DK2 spectrophotometers. Gas-chromatographic analyses were carried out on a Perkin–Elmer model 101 gas chromatograph as described previously[17].

Chemicals

Phenylacetylene (Fluka) was distilled before use. Complexes (I), (II), (III), (IV), (V) were prepared by known methods[5–8]. Preparations of (VI) and (VII) are described in the preceding paper[18].

Polymerization reactions were carried out by adding the monomer (5–10 ml) to the complex (100–400 mg) in a three-necked reaction flask equipped with mechanical stirrer, thermometer and condenser. A silicone oil bath was used for reactions at high temperatures.

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REFERENCES

1 C. W. Bird, *Transition Metal Intermediates in Organic Synthesis*, Academic Press, Logos Press, 1967, p. 1.
2 F. L. Bowden and A. B. P. Lever, *Organometal. Chem. Rev.*, 3 (1968) 227.
3 L. S. Meriwether, M. F. Leto, E. C. Colthup and G. W. Kennerly, *J. Org. Chem.*, 27 (1962) 3930.
4 J. Chatt, G. A. Rowe and A. A. Williams, *Proc. Chem. Soc.*, (1957) 208.
5 K. A. Jensen, *Z. Anorg. Allg. Chem.*, 229 (1936) 265.
6 A. D. Allen and M. C. Baird, *Chem. Ind. (London)*, (1935) 139.
7 F. Cariati, R. Ugo and F. Bonati, *Inorg. Chem.*, 5 (1966) 1128.
8 F. Bonati, Private communication.
9 Y. Okamoto, A. Gordon, F. Movsovicius, H. Hellmon and W. Brenner, *Chem. Ind. (London)*, (1961) 2004.
10 A. A. Berlin, *J. Polym. Sci.*, 55 (1961) 621.
11 V. V. Korshak, A. M. Polyakova and M. D. Sudikava, *Vysokomol. Soedin.*, 2–8 (1960) 1246.
12 P. Ehrlich, R. J. Kern, E. D. Pierron and T. Provder, *J. Polym. Sci.*, *Part B*, 5 (1967) 911.
13 R. J. Kern, Preliminary communication.
14 A. A. Berlin, M. J. Cherkashin, Y. G. Aseyev and I. M. Shcherbakova, *Vysokomol. Soedin*, 6 (1964) 1773.
15 A. A. Berlin, M. J. Cherkashin, P. P. Kisilitsa and O. N. Pigorov, *Vysokomol. Soedin*, 9 (1967) 1835.

16 A. A. BERLIN, M. J. CHERKASHIN, I. P. CHERNYSHEVA, Y. G. ASEYEV AND E. I. BARKAN, *Vysokomol. Soedin.*, 9 (1967) 1840.
17 A. FURLANI DONDA AND G. MORETTI, *J. Org. Chem.*, 31 (1966) 985.
18 I. COLLAMATI AND A. FURLANI, *J. Organometal. Chem.*, 17 (1969) 457.