Applied Organometallic Chemistry (1987) 1 555–563

02682605/87/01609555/$03.50

Linear trimerization of 1-ethynylcyclohexan-1-ol catalysed by nickel(II) complexes

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Received 31 July 1987 Accepted 24 August 1987

The catalytic reaction of 1-ethynylcyclohexan-1-ol (EC) in the presence of bisphosphine nickel(II) complexes yields a linear trimer. The trimer could be isolated and characterized by means of MS, IR and NMR spectroscopies. The reaction mechanism is also discussed.

Keywords: Trimerization, 1-ethynylcyclohexan-1-ol linear trimer, Ni(II) catalysis.

INTRODUCTION

New synthetic methods which convert small organic molecules into products of greater complexity have been the object of many investigations. Among them, cycloaddition reactions have drawn a great deal of attention, as reported in a recent review by Vollhardt.[1] The interest in the synthesis of benzene derivatives from functionalized alkynes arises from their potential use as starting materials for the building up of more complex organic molecules with biological interest.[2] Furthermore, linear attachment of alkynes gives polymers with conductive behavior.

Some years ago we investigated the catalytic activity of a series of $[NiX_2L_2]$ complexes (X = Cl, Br, I, NCS, NO_3; L = phosphines), with monosubstituted acetylenes, $HC{\equiv}CR$,[4–6] in order to determine the influence of the ligands on the reaction mechanism. The results showed that the catalytic activity of various complexes is dependent on the phosphines, on the anions and on the R group of the alkyne monomer.

On the basis of the reaction mechanism proposed by Meriwether,[7] who studied similar catalytic reactions, and of our results, we proposed as the active intermediates $[NiX(C{\equiv}CR)L_2]$ complexes ($R = -C_6H_5$, $-C(CH_3)_2OH$).[6,8] We have now examined the influence of a new substituent (1-ethynylcyclohexan-1-ol, EC; $R = -C_6H_{10}OH$) on the alkyne molecule $HC{\equiv}CR$ in reactions catalysed by $[Ni(NCS)_2L_2]$ and $[Ni(NCS)(C{\equiv}CR)L_2]$ complexes (L = PPh_3, PBu_3): owing to the steric hindrance of the $-C_6H_{10}OH$ group, a linear trimer of EC instead of the cyclic one is isolated as the main reaction product in the presence of the $[Ni(NCS)(C{\equiv}CR)L_2]$ complexes. The characterization and the study of the monomer sequence in a short linear molecule can be very useful as a model for enchainment in the polymer backbones. The problem of the actual chain structure of polymers obtained from monosubstituted acetylenes has not been clearly solved yet.[9–14] Therefore we believe that the linear trimer of EC that we have now obtained and characterized might be a starting point to the understanding of the structure of polymer molecules and of the polymerization mechanism.

EXPERIMENTAL

Reactions

(1) $[Ni(NCS)(C{\equiv}C{-}C_6H_{10}OH)(PPh_3)_2]$ or $[Ni(NCS)(C{\equiv}C{-}C_6H_{10}OH)(PBu_3)_2]$ (200 mg; approx. 0.251 mmol), prepared following previously reported methods,[15] was refluxed with 5 cm^3 (40.3 mmol) of 1-ethynylcyclohexan-1-ol (EC) (Fluka, commercial product) in the presence of 15 cm^3 of benzene as the reaction solvent (Carlo Erba, analytical purity grade) for 48 h. The amount of unreacted EC was checked during the reaction by gas chromatographic analysis (GC). The final solution was evaporated to a small volume and cooled overnight at 0°C: white microcrystals (TCE, i.e. trimeric EC) precipitated and were filtered off. The white microcrystals were crystallized by several

organic solvents (benzene, chloroform, toluene) and acetone/water (see discussion); yields were 30% from the catalyst $[Ni(NCS)(C{\equiv}C_6H_{10}OH)(PPh_3)_2]$; 15% from the catalyst $[Ni(NCS)(C{\equiv}C_6H_{10}OH)(PBu_3)_2]$.

Elemental analysis. TCE crystallized from acetone/water: Found, C 74.45; H 9.33. Calcd. for $3(C_8H_{12}O)H_2O$, C 73.81, H 9.81%. TCE crystallized from benzene: Found C 77.18, H 9.77; Calcd. for $(C_8H_{12}O)_3$, C 77.38, H 7.97%. The melting points of TCE (measured by a Kofler apparatus) depend on the crystallization solvents: (a) m.p. 85–88°C (benzene); (b) m.p. = 123–128°C (acetone–water).

(2) $[Ni(NCS)_2(PPh_3)_2]$ or $[Ni(NCS)_2(PBu_3)_2]$ (200 mg; 0.30 mmol) dissolved in C_6H_6 (15 cm^3) was refluxed in the presence of EC (5 cm^3, 40.3 mmol) for 72 h and 48 h respectively. The unreacted EC was checked by gas chromatography during the reaction time. $[Ni(NCS)_2(PPh_3)_2]$ gave 30% yield of 1,3,5-tris(1-hydroxycyclohexyl)benzene (TCEB), while for $[Ni(NCS)_2(PBu_3)_2]$ the TCEB yield was 15%. The formation of the cyclic trimer was found in the reaction mixture by GC whilst no traces of TCE were detected.

Apparatus

The GC analyses were performed on a Perkin–Elmer 900 instrument using stainless-steel columns, length 2 m, i.d. 2.5 mm, filled with SE 30 (10%) on Chromosorb 60–80 mesh; column, detector, and injector temperatures were 70°C, 100°C, and 150°C, respectively.

The IR spectra were run on a Perkin–Elmer 580B instrument (Nujol mulls), the UV spectra on a Beckmann DK2A, MS spectra on an AEI MS 12 at 70 eV and 150°C, and the ^1H and ^{13}C NMR spectra on a Varian 300 MHz using TMS as internal standard.

RESULTS AND DISCUSSION

In previous studies it was found that the complex $[NiBr_2(PBu_3)_2]$ gives 1,3,5-trisubstituted cyclic trimers of many acetylenic alcohols including 1,3,5-tris(1-hydroxycyclohexyl)benzene (TCEB) amongst these,[4] while the 1,2,4-trisubstituted TCEB was never isolated. As an extension of our studies on the cyclotrimerization reactions of monosubstituted acetylenes we compared the catalytic activity of $[Ni(NCS)_2L_2]$ and $[Ni(NCS)(C{\equiv}CR)L_2]$ complexes (R = $-C_6H_5$, $-C(CH_3)_2OH$). We found that monoacetylide complexes could be the active intermediates, as proposed, because the induction period was noticeably reduced and the same final distribution of products was obtained.[8]

Now we have investigated the reactivity of the $[Ni(NCS)_2L_2]$ and $[Ni(NCS)(C{\equiv}C{-}C_6H_{10}OH)L_2]$ ($L = PPh_3, PBu_3$) complexes with the aim of studying the influence of bulky hydroxyalkyl substituents on the acetylene. The $[Ni(NCS)_2L_2]$ catalysts give 1,3,5-TCEB in 30% yield ($L = PPh_3$) or 15% yield ($L = PBu_3$).

When the monoacetylide complexes are refluxed in the presence of EC a different product (TCE) is isolated by cooling the reaction mixture at 0°C. The crude solid is purified with petroleum ether and by chromatography on a silica (70–230 mesh) column, eluent benzene; further crystallizations from various solvents ($CHCl_3$/n-hexane, CCl_4, C_6H_6, CH_3COCH_3/H_2O) have been performed. The mass spectrum gives $|M^+| = 372\,m/z$ which corresponds to a molecule obtained from three monomer units. Other peaks at $m/z = 354$ ($M^+ - H_2O$), $m/z = 336$ ($M^+ - 2H_2O$), $m/z = 318$ ($M^+ - 3H_2O$) are observed deriving from the dehydration of the trimer, and $m/z = 107$ ($CH{=}CH{-}C_6H_9$), $m/z = 105$ ($C{\equiv}C{-}C_6H_9$), $m/z = 91$ ($C{\equiv}C{-}C_5H_7$), $m/z = 81$ (C_6H_9), are characteristic fragments of the monomer unit. The IR spectra of TCE show a different pattern depending on the crystallization procedure: C_6H_6 gives a microcrystalline product which exhibits a broad strong band at 3380 cm^{-1} due to the O–H stretching mode, a very weak band at 2200 cm^{-1} due to C≡C stretching and low absorptions in the range 1700–1600 cm^{-1} (Fig. 1A). If the product crystallized from C_6H_6 is recrystallized from $CHCl_3$/n-hexane, CH_3COCH_3/petroleum ether or CH_3COCH_3/H_2O, the spectrum changes giving three bands at 3580, 3400, 3200 cm^{-1} (ν O–H), the band at 2200 cm^{-1} becomes more intense and a new strong band appears at 1650 cm^{-1}, which can be attributed to conjugated double bonds; the range 1300–1600 cm^{-1} is also remarkably modified (Fig. 1B). However when the product is crystallized again from C_6H_6, it returns to the former conformation. The cyclic 1,3,5-TCEB does not undergo the same modifications when crystallized in the same sequence. Therefore hydrogen bonds between the OH groups of the molecule (which are in different chemical environments) with polar

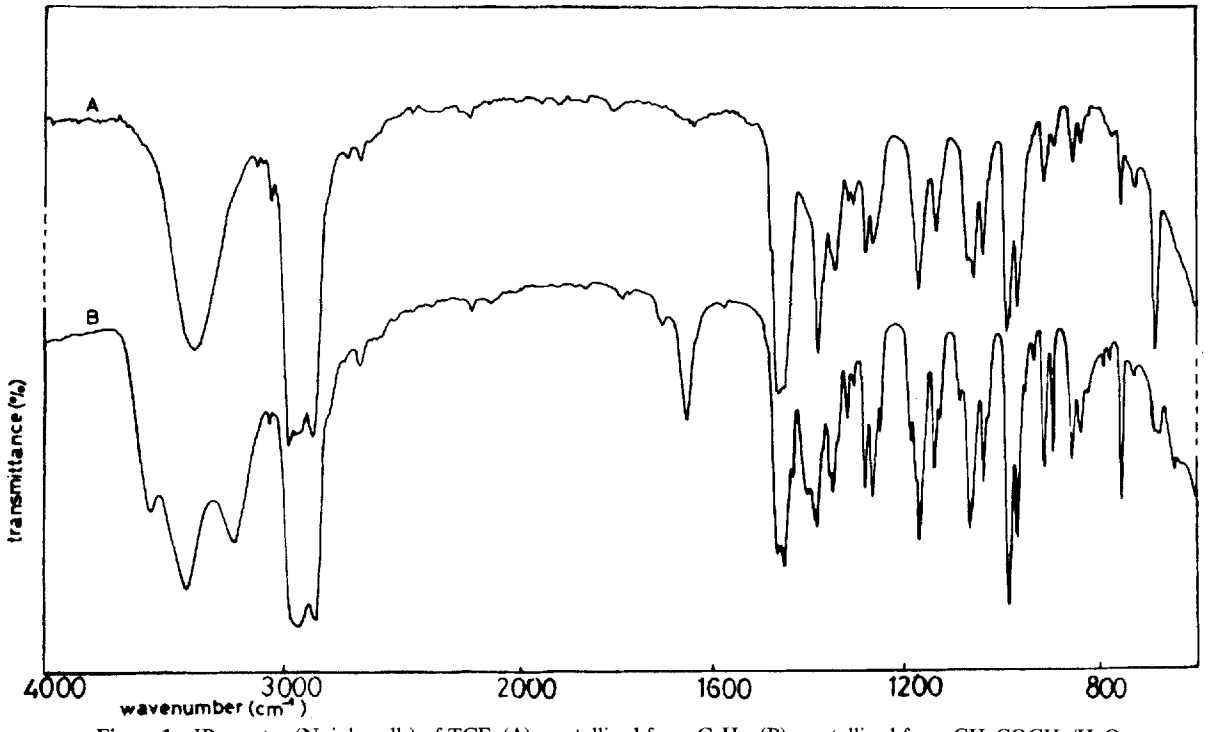


Figure 1 IR spectra (Nujol mulls) of TCE: (A) crystallized from C_6H_6; (B) crystallized from CH_3COCH_3/H_2O.

solvent molecules can occur, leading to modifications of the lattice as was observed for the cyclic cotrimer 1,3-(1-hydroxy-1-methylethyl)-5-(1-hydroxycyclohexyl)benzene.[16] In solution the same conformation is obtained as shown by the UV and NMR spectra. All the samples crystallized from different solvents in C_2H_5OH solution exhibit the spectrum given in Fig. 2; the UV spectrum of 1,3,5-TCEB is also reported (Fig. 2).

^{1}H and ^{13}C NMR spectra

In order to state the structure of TCE a series of ^{1}H and ^{13}C NMR spectra were run on the monomer EC, on the symmetric cyclic trimer (TCEB) and on the new product (TCE), which on the basis of mass and IR spectra was considered to be a linear trimer rather than the 1,2,4-tris(1-hydroxy-1-cyclohexyl)benzene.

In Fig. 3 we give the ^{1}H and ^{13}C NMR spectra of EC. In the ^{1}H NMR spectrum broad signals are observed in the range 1.2–1.9 ppm due to the cyclohexane ring protons. The singlet at 2.83 ppm is attributed to the alkyne proton and the OH group gives the singlet at 4.3 ppm (Fig. 3A). The ^{13}C NMR spectrum of EC (Fig. 3B) can be interpreted by comparison with the spectra of butynol (X), methylcyclohexanol (Y) and cyclohexanol (Z) (see Table 1). The ^1J CH coupling constants (Fig. 3C) are in agreement with the literature values and confirm the proposed assignments.[17] The ^{13}C NMR spectrum of TCEB reveals the symmetrical structure of the product (Fig. 3D). By comparison with the values reported for 1,3,5-trisubstituted benzene derivatives,[17] the signal at 119.93 ppm is attributed to the unsubstituted carbon atoms, and the signal at 150.64 ppm is due to those carbon atoms of the benzene ring to which no hydrogen atoms are bonded. The signal at 73.31 ppm is again due to the carbon atoms of the cyclohexane rings to which no hydrogen atoms are bonded. The positions of the other signals (39.87; 26.44; 22.89 ppm) are in agreement with those of the other cyclohexanol derivatives (see Table 1).

From the ^{1}H and ^{13}C NMR spectral data we propose for TCE the structure reported in Fig. 4. The ^{1}H NMR spectrum (Fig. 5A) reveals signals in the range 5.7–6.7 ppm which are indicative of protons bonded to non-aromatic sp^2 carbon atoms. The coupling constant ^3JHH (15 Hz) of the signals at 5.84–5.79 ppm reveals the existence of two protons in *trans*(*E*) positions on a double

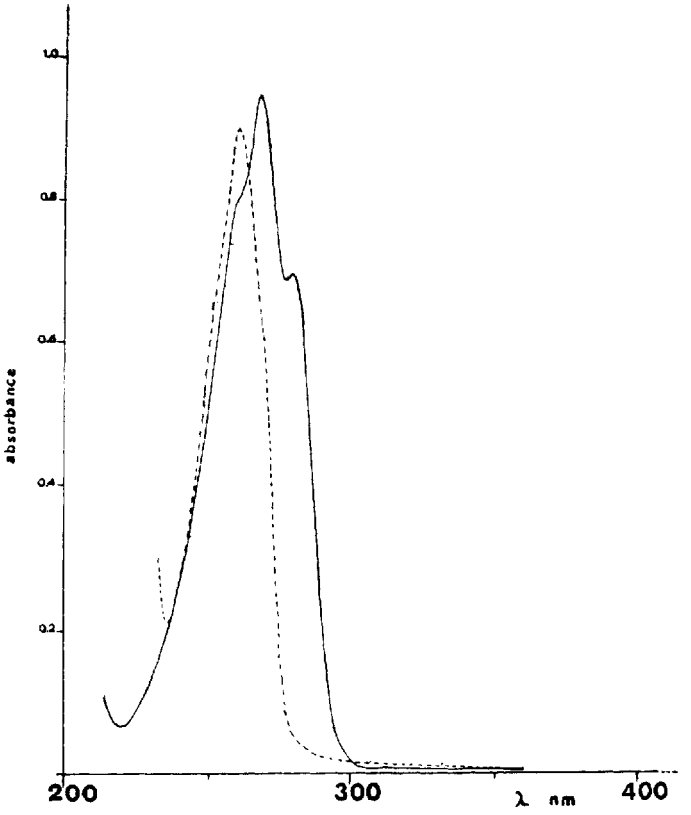


Figure 2 UV spectra (solvent CH_3OH) of TCE (solid line) and TCEB (broken line).

bond. In the ^{13}C NMR spectrum (Fig. 5B) we observe 18 signals which indicate the low symmetry of the molecule, if compared with the ^{13}C NMR spectrum of TCEB in which only six signals (four carbon atoms of the three equivalent cyclohexane groups and two for the two kinds of carbon atoms of the symmetric benzene ring) were observed.

By varying the pulse width we have seen that the intensity of the signals at 68.86, 71.20, 73.61, 81.64, 102.86 and 133.64 ppm is noticeably reduced; therefore these signals must be due to carbon atoms to which no hydrogen atoms are attached. This assignment was confirmed by a series of coupled spectra. We have observed that the signal at 144.97 ppm (Fig. 5C) is split into a doublet (^1J CH = 151.5 Hz), the signal at 132.56 ppm gives a doublet at 131.54 and 133.53 ppm (^1J CH = 158.7 Hz), and the signal at 126.1 ppm is also split into a doublet (^1J CH = 155 Hz). Therefore these signals can be attributed to olefinic carbon atoms bonding only one hydrogen atom.

The long-range couplings are shown in Fig. 5D. We observed that the signal at 81.64 ppm is doubled (^2J CH = 11.6 Hz); this signal can be attributed to the C(8) *sp* carbon atom of the TCE (Fig. 4) molecule. The coupling constant ^2J is rather high, but the planarity due to the conjugation of the system between the C(7)–C(10) carbon atoms may enhance the ^2J CH coupling constant value.

Further splittings of the various signals are observed in the enlarged spectra (Fig. 5E). The J values are about 1–2 Hz and are due to long-range couplings. The signal at 126.1 ppm still remains a doublet: therefore it is attributed to the C(9) carbon atom which is coupled with the directly bonded hydrogen (^1J CH = 155 Hz). The C(11) carbon atom, to which the signal at 132.56 ppm corresponds, is coupled with the directly bonded hydrogen (^1J CH = 158.7 Hz), with the hydrogen bonded to the C(12) carbon atom (^2J CH = 1.8 Hz) and with the hydrogen bonded to the C(9) carbon atom (^3J CH = 7.9 Hz). No long-range coupling is observed

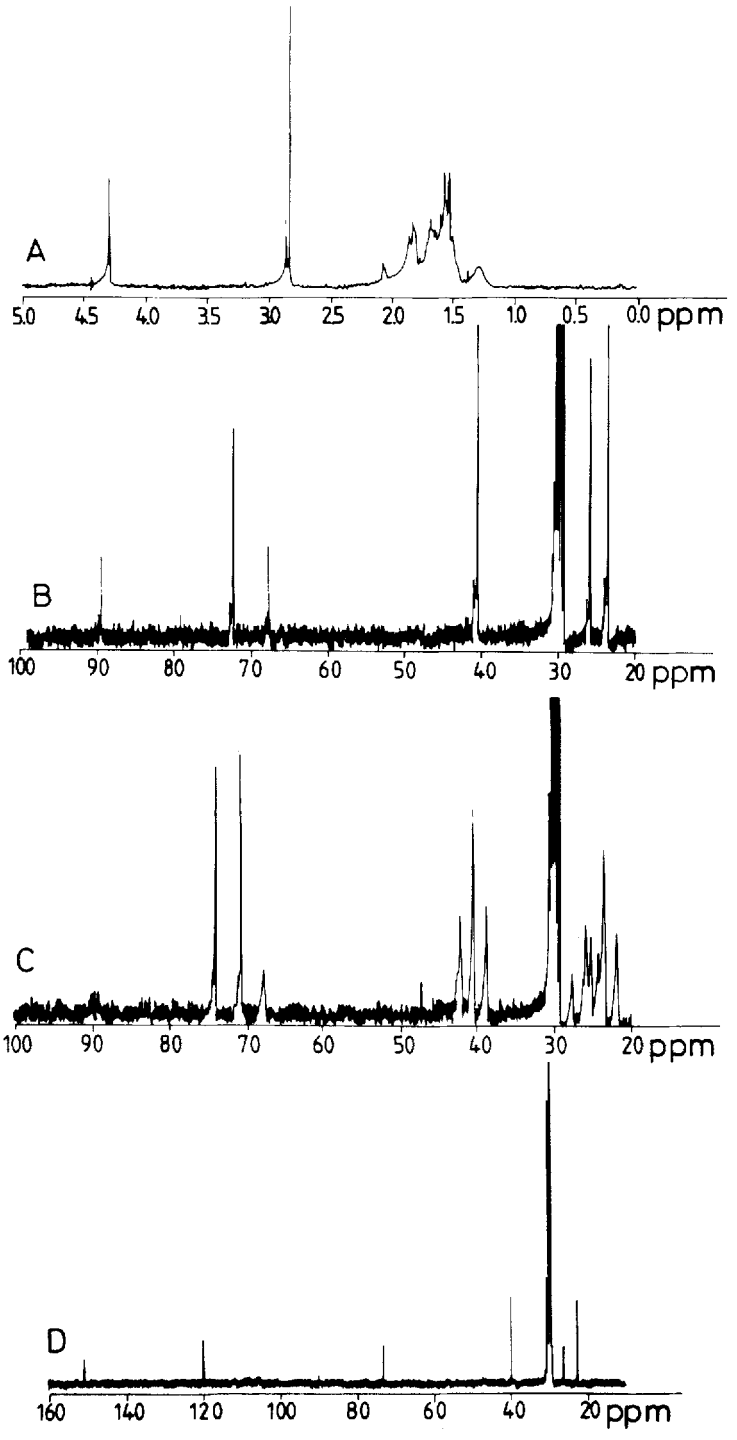
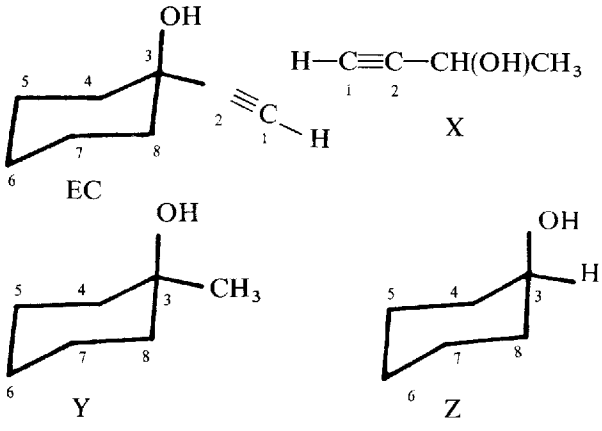


Figure 3 (A) ^{1}H NMR spectrum of EC; (B) ^{13}C NMR spectrum of EC (solvent CD_3COCD_3); (C) ^{13}C NMR coupled spectrum of EC (solvent CD_3 $COCD_3$); (D) ^{13}C NMR spectrum of TCEB (solvent CD_3COCD_3).

Table 1 ^{13}C NMR spectra of 1-ethynylcyclohexan-1-ol (EC), but-1-yn-3-ol (X),[a] 1-methylcyclohexan-1-ol (Y)[a] and cyclohexan-1-ol (Z)[a]



EC			X	Y	Z
δ_C(ppm)	J CH(Hz)	Carbon atom		δ_C(ppm)	
23.61	125.9	5–7		22.8	24.4
25.92	121.5	6		26.0	25.9
40.58	137.2	4–8		39.7	35.5
67.81	—	3		69.0	69.5
72.44	24.88	1	72.0		
89.45	—	2	86.8		

[a]The ^{13}C chemical shifts of X, Y, Z are taken from Ref. 17 (X = no. 1197; Y = no. 473; Z = no. 474).

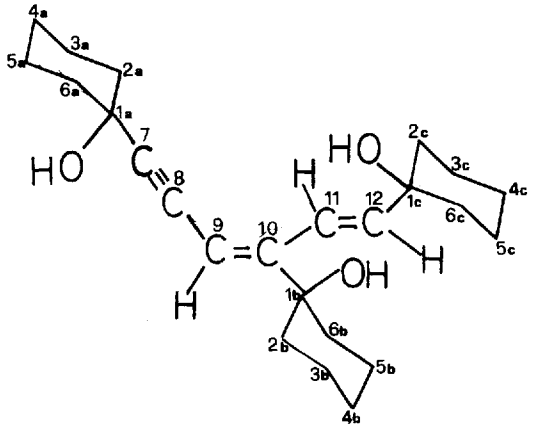


Figure 4 Structure of TCE molecule.

between the C(9) carbon atom and the hydrogen bonded to the C(11), perhaps as a consequence of a possible rotation of the molecule around the C(10)–C(11) bond.

The signal at 144.97 ppm is due to the C(12) carbon atom. In fact the signals of the doublet are further split into multiplets owing to possible long-range couplings with the protons of the cyclohexane ring. When we irradiated in the corresponding position of the doublet at 5.79–5.84 ppm of the ^1H NMR spectrum, in the coupled ^{13}C NMR spectrum the doublet at 145.95 and 143.9 ppm was seen as a singlet at 144.97 ppm. Therefore the doublet of the ^1H NMR spectrum is due to the hydrogen bonded to the C(12) carbon atom. The multiplet in the ^1H NMR spectrum in the range 6.5–6.7 ppm (Fig. 5A) is due to the protons bonded to the C(9) and C(11) carbon atoms of the TCE molecule.

In the ^{13}C NMR spectrum of Fig. 5B the signal at 102.87 ppm is due to the C(7) *sp* carbon atom, and the signal at 133.64 ppm to the C(10) sp^2 carbon (two carbon atoms which are not bonded to hydrogen). The other signals, due to the three non-equivalent cyclohexane rings, are in the expected range (Table 1).

CONCLUSIONS

The structure of the linear trimer TCE has been proposed (Fig. 4) by means of NMR spectroscopy because single crystals of the product for X-ray analysis could not be obtained. The nature of the alkyne moiety is one factor amongst others (reaction conditions, type of phosphine, metal atom of the catalyst) which interferes in the reaction pathway. The TCE molecule shows a *cis*–transoidal head–tail sequence for two units, while the third one is bonded through tail–tail bonding. The reaction mechanism proposed for the formation of the TCE molecule is shown in Fig. 6. The monomer molecules are activated by coordination on the nickel atom. As was found for other catalysts in polymerization reactions,[12] a *cis* opening of the triple bond occurs; than an insertion of the activated molecule into the Ni–C σ-bond takes place. The insertion of the second acetylene molecule originates a *cis*-transoidal structure of the growing chain, while the third monomer unit

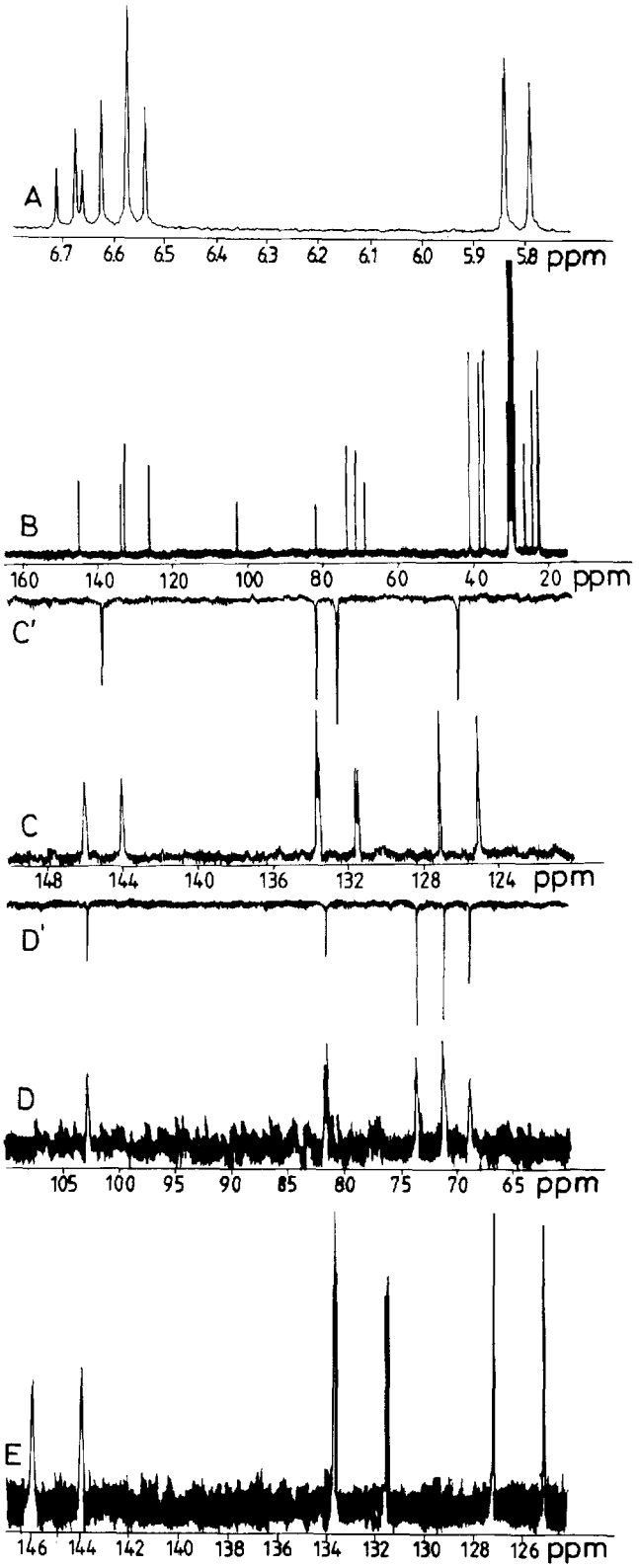


Figure 5 NMR spectra of TCE: (A) ^{1}H NMR (solvent $CDCl_3$); (B) ^{13}C NMR (solvent CD_3COCD_3); (C), (D), (E) ^{13}C NMR coupled spectra; (C'), (D') ^{13}C NMR decoupled spectra.

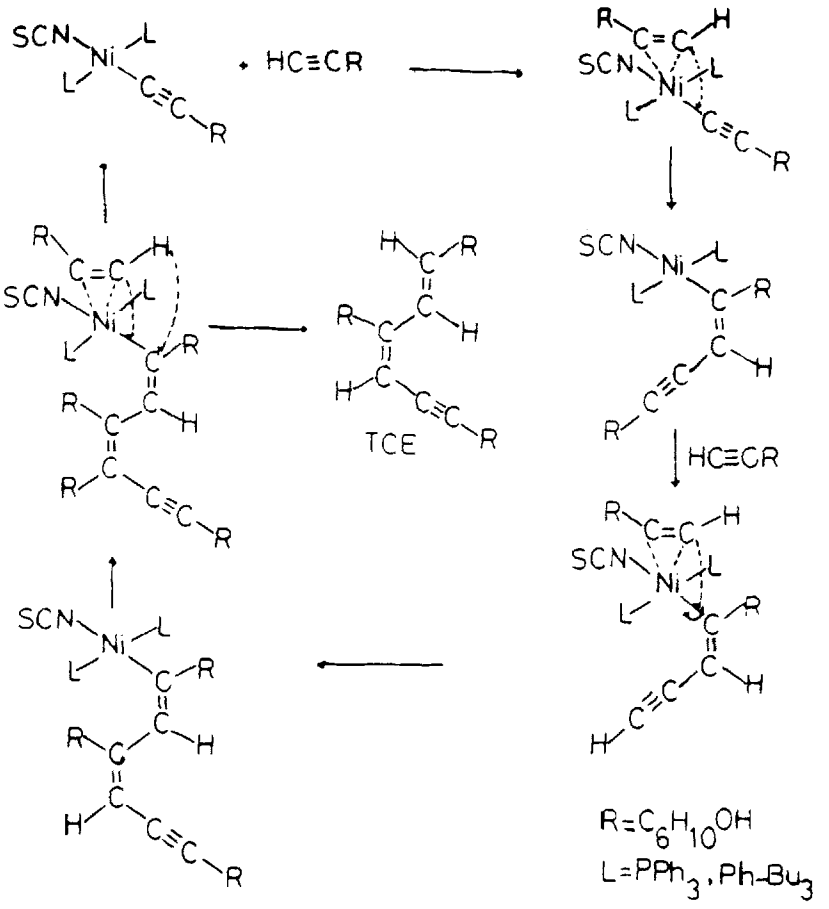


Figure 6 Proposed reaction mechanism.

reproduces the catalyst by hydrogen transfer to the leaving linear trimer.

The $[Ni(NCS)_2L_2]$ complexes give the cyclic trimer 1,3,5-TCEB. The formation of 1,3,5- or 1,2,4-cyclic trimers requires that the insertion of the π-coordinated acetylene molecule into the Ni–C σ-bond of the acetylide complex originates a *cis*–cisoidal sequence. However, when the substituent on the acetylene is $-C_6H_{10}OH$, with a high steric hindrance, the active intermediate for the aromatization reaction is not the $[Ni(NCS)(C{\equiv}CR)L_2]$ complex, which still leads to a '*cis*' opening of the triple bond of the acetylene, but the insertion reaction is followed by a *cis*–transoidal propagation. In the case of phenylacetylene and 2-methylbut-3-yn-2-ol that we have previously examined,[8] we found that the $[Ni(NCS)(C{\equiv}CR)L_2]$ complex gives the same products as the $[Ni(NCS)_2L_2]$ complexes. Therefore a general conclusion cannot be drawn for these catalytic systems. It seems proved however, that the '*cis*' opening of the triple bond, activated by the nickel complexes, gives *cis*–cisoidal or *cis*–transoidal attachments. Molecules of the polymeric fractions, which are in part formed in such reactions, should therefore exhibit analogous steric structures.

The polymers of EC, which contain a backbone of alternate C=C double bonds like polyacetylene are suitable for the preparation of conducting materials after doping. Knowledge of the real structure of the polymer chain, which should be analogous to that of the linear trimer, is therefore of great importance for development of an understanding of chain–dopant interactions and of conducting mechanisms.

Acknowledgements The authors wish to thank CNR, Progetti Finalizzati Chimica Fine e Secondaria, Italy for financial support.

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