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Polymerization of phenylacetylene catalysed by cyclopentadienylnickel complexes†

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A wide range of cyclopentadienylnickel compounds catalyse the reaction of phenylacetylene under solvent-free conditions, giving a mixture of cyclotrimers, linear oligomers and poly(phenylacetylene). No reaction is observed in the case of internal acetylenes. Cyclotrimer formation is favoured by the presence of cyclopentadienylnickel catalysts bearing a chloro substituent at nickel. A reduction in reaction temperature results in lower conversion but favours linear oligomer and polymer formation. The main effect of the presence of solvent, regardless of whether it is potentially coordinating (toluene) or not (*n*-octane), is to suppress almost completely reactions catalysed by nickelocene. Copyright © 2001 John Wiley & Sons, Ltd.

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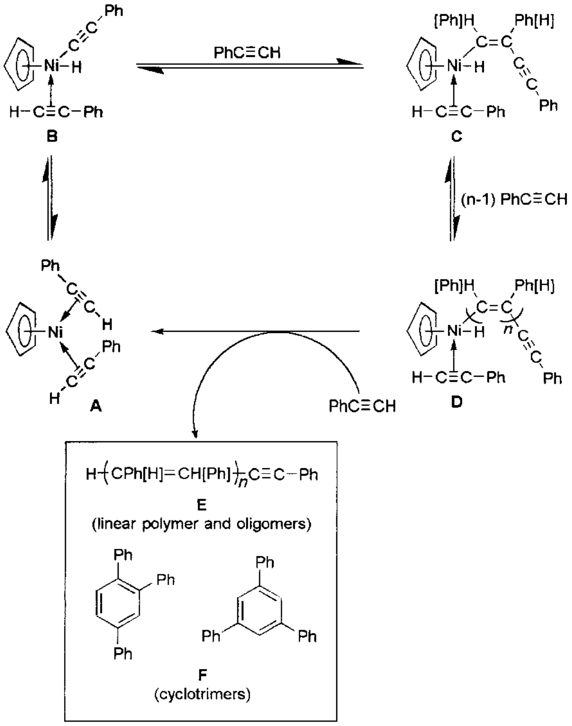
Nickelocene catalyses the polymerization of terminal acetylenes in the absence of solvent, giving, in the case of phenylacetylene, a mixture of cyclotrimers, linear oligomers and *trans-cisoidal* poly(phenylacetylene) with 92% conversion after 6 h at 115 °C.[1,2] Here it is reported that a wide variety of cyclopentadienylnickel complexes also catalyse these reactions and that the nature and distribution of the products can be monitored by size exclusion chromatography (SEC).

The $(Ph_3P)_2Ni(CO)_2$-catalysed polymerization of acetylenes in solution was reported many years ago,[3] the suggested mechanism [Scheme 1 with $(Ph_3P)_2$ in place of (η-Cp)] accounting for both linear polymerization and cyclotrimerization.[4]



Scheme 1 Reaction mechanism for polymerization and cyclotrimerization of phenylacetylene catalysed by [CpNi] complexes in the absence of solvent.

In order to investigate the feasibility of using SEC for monitoring the polymerization reaction, the polymerization of phenylacetylene in the presence of nickelocene was repeated under the same conditions as those used previously when the reaction products were separated and analysed.[2] The SEC trace showed four peaks (Fig. 1) corresponding to the four components previously separated from the reaction mixture and characterized:[2] (i) retention time 32.01 min; *trans-cisoidal* poly(phenylacetylene) (M_w *ca* 3000, polydispersity 1.6); (ii) 40.30 min, linear oligomers of phenylace-

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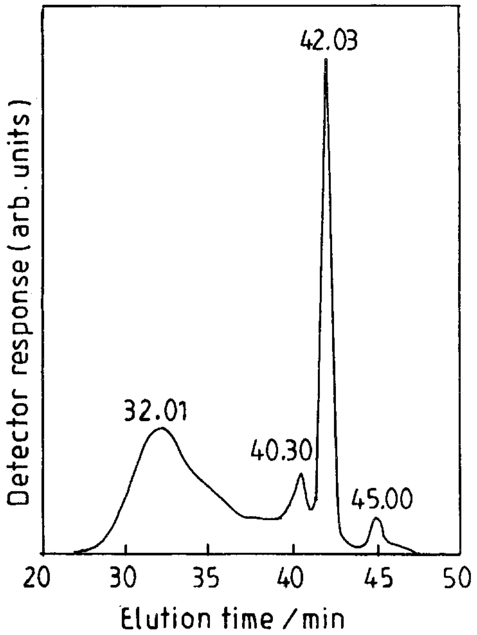
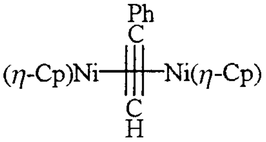


Figure 1 SEC trace for product mixture from reaction of phenylacetylene in the presence of nickelocene under the standard conditions.

tylene (that with $n = 4.5$ has been previously isolated[2]), (iii) 42.03 min; 1,2,4- and 1,3,5-triphenylbenzene, and (iv) 45.00 min, unchanged phenylacetylene. No coincidence of retention times for various other possible products, including tetraphenylcyclooctatetraene isomers[5] and $PhC{\equiv}C{-}CH{=}CHPh$,[6] was found.

No reaction of internal acetylenes ($Me_3SiC{\equiv}CSiMe_3$, $PhC{\equiv}CSiMe_3$, $PhC{\equiv}CPh$) occurred under solvent-free conditions in the presence of nickelocene or the other cyclopentadienylnickel catalysts. This suggests that, as with $(Ph_3P)_2Ni(CO)_2$, the reaction mechanism includes an acetylene hydrogen transfer step rather than involving nickelole or other such intermediates.[7,8] The mechanism probably operating in this case is that of Meriwether (Scheme 1), the catalytic species **A** being formed by loss of a cyclopentadienyl ring, a reaction which is known to occur readily.[9,10] The following step in the catalytic cycle is the oxidative addition of phenylacetylene giving **B**, such intermediate ethynyl hydride complexes of nickel having been previously isolated.[11] The next step is the insertion of phenylacetylene into the Ni—C bond, a reaction that has been previously observed.[12–14] This step is repeated ($n-1$)-fold giving **D** which re-forms **A** by reductive elimination of linear polymer **E**. The cyclotrimers **F** can be formed by reductive elimination from **D** when $n = 2$.

Table 1 Product distribution from catalysed solvent-free polymerization of phenylacetylene[a]

	Product mixture composition[b]			
Catalyst	Polymer (%)[c]	Linear oligomers (%)[d]	Cyclotrimers (%)[e]	$PhC{\equiv}CH$ (%)[f]
 $(\eta\text{-Cp})Ni(\mu\text{-}PhC{\equiv}CH)Ni(\eta\text{-Cp})$	53	7	30	8
$[(\eta\text{-Cp})Ni(CO)]_2$	40	20	35	8
(η-Cp)NiNO	23 (1[g])	2(3[g])	11 (1[g])	65(95[g])
(η-Cp)Ni($GeBr_3$)(Co)	26	0	15	59
(η-Cp)Ni($PBu^n{}_3$)I	56	8	29	8
(η-Cp)Ni[$P(OMe)_3$]Cl	38	15	40	3
(η-Cp)Ni(PPh_3)Cl	52	1	38	7
$(PPh_3)_2Ni(CO)_2$	35	0	60	6

[a] Catalyst (*ca* 0.01 mmol) and phenylacetylene (9.1 mmol) heated at 115 °C for 6 h.
[b] Determined by SEC.
[c] Retention time 31.83–32.22 min.
[d] Retention time 39.19–40.3 min.
[e] Retention time 42.03 min
[f] Retention time 45.00 min.
[g] Reaction temperature 65 °C.

In order to investigate the effect of solvents, the nickelocene-catalysed reaction was carried out at 100 °C for 7 h in the presence of 5 ml of toluene or *n*-octane giving 8% and 5% overall reaction, respectively. The main effect of the presence of solvent, regardless of whether it is potentially coordinating (toluene) or not (*n*-octane), is to suppress almost completely reactions catalysed by nickelocene. In the case of nickelocene, coordination of a solvent molecule occurs at the expense of an acetylene molecule in the 19-electron catalytic species **A** (Scheme 1) thus inhibiting the reaction.

Use of the green phenylacetylene-bridged binuclear compound $[(\eta\text{-Cp})Ni]_2(PhC{\equiv}CH)$ or the carbonyl-bridged binuclear complex $[(\eta\text{-Cp})Ni(CO)]_2$ gave results very similar to those with nickelocene. In the case of $[(\eta\text{-Cp})Ni(CO)]_2$ most probably the known reaction[15] to give $[(\eta\text{-Cp})Ni]_2(PhC{\equiv}CH)$ takes place initially. Indeed, when the internal acetylene PhC≡CPh was treated with 0.35 mol% $[(\eta\text{-Cp})Ni(CO)]_2$ at 115 °C in the absence of solvent, the initially red solution turned deep green within 2 min consistent with the formation of $[(\eta\text{-Cp})Ni]_2(PhC{\equiv}CPh)$ (no oligomerization of the acetylene was observed). Most probably the nickelocene-catalysed reaction involves an initial conversion step to give $[(\eta\text{-Cp})Ni]_2(PhC{\equiv}CH)$, which then subsequently forms the catalytic species **A** (Scheme 1).

The complex $(\eta\text{-Cp})Ni(NO)$ gives only 35% conversion at 115 °C. A Decrease in the reaction temperature to 65 °C results in a reduction both in the extent of reaction (to 5%) and, as with nickelocene, in the proportion of cyclotrimer in the product mixture. Loss of the NO ligand enabling formation of $[(\eta\text{-Cp})Ni]_2(PhC{\equiv}CH)$ occurs only with difficulty. Indeed, it has been found that nitrosyl exchange with ^{15}NO did not occur for $(\eta\text{-Cp})Ni(NO)$ in 10 days at 120 °C.[16]

The complex $(\eta\text{-Cp})Ni(GeBr_3)(CO)$ gave very similar results to those for $(\eta\text{-Cp})Ni(NO)$, suggesting that although the CO ligand is readily lost (as shown by the initially green solution turning orange–red after only 1 min at 115 °C), the presence of the electron-withdrawing $GeBr_3$ substituent[17] hinders subsequent reactions with phenylacetylene. The reaction mechanism may involve 20-electron species [Scheme 1 with $(\eta\text{-Cp})(GeBr_3)$-Ni in place of $(\eta\text{-Cp})Ni$]. No reaction was observed with PhC≡CPh.

In the case of $(\eta\text{-Cp})Ni(Bu^n{}_3P)I$, the reaction mixture did not pass through a green stage and here too the reaction mechanism may involve 20-electron species [Scheme 1 with $(\eta\text{-Cp})NiI$ in place of $(\eta\text{-Cp})Ni$].

The complexes $(\eta\text{-Cp})Ni[P(OMe_3)]Cl$ and $(\eta\text{-Cp})Ni(Ph_3P)Cl$ gave very similar results, the product mixtures being much richer in cyclotrimers than in the case of nickelocene. Since the phosphorus ligands are quite different in nature,[18] the phosphine groups are probably not present in the active catalytic species. The reaction mechanism in each case may involve 20-electron species [Scheme 1 with $(\eta\text{-Cp})NiCl$ in place of $(\eta\text{-Cp})Ni$]. Indeed, in neither case was a green stage observed corresponding to formation of $[(\eta\text{-Cp})Ni]_2(PhC{\equiv}CH)$.

Finally, for comparison, the effect of $(Ph_3P)_2Ni(CO)_2$ was investigated in the absence of solvent. Unlike the reaction in benzene, where only cyclotrimer and linear trimer are afforded,[19] the solvent-free reaction of phenylacetylene in the presence of $(Ph_3P)_2Ni(CO)_2$ gives linear polymer in addition to cyclotrimer, consistent with the much greater concentration of phenylacetylene favouring a larger value of n in intermediate **D** [Scheme 1 with $(Ph_3P)_2$ in place of $(\eta\text{-Cp})$]. No reaction was observed with PhC≡CPh.

It can be concluded that under solvent-free conditions cyclopentadienylnickel compounds, in general, are active catalysts for the polymerization of terminal acetylenes.

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