A Novel Polymerisation involving C–H Addition to C≡C catalysed by $RhCl(Ph_3P)_3$

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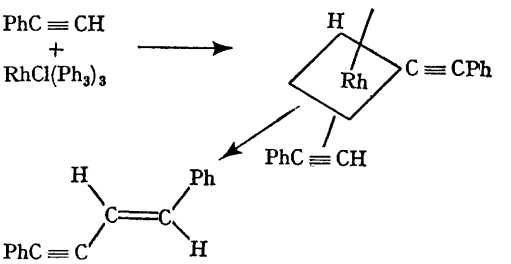
$RhCl(Ph_3P)_3$ catalyses formation of a poly(phenylacetylene)[1] differently from those types initiated thermally or with Zeigler-type catalysts (for example, di-isobutylaluminium hydride–ferric acetylacetonate). The product is believed to contain conjugated unsaturation almost entirely *trans* with respect to the chain. This Communication assembles evidence that under the influence of $RhCl(Ph_3P)_3$ phenylacetylene behaves as a bifunctional monomer. The triple bond acts as one function, the C–H bond is the second. Propagation proceeds by cumulative additions of the C–H function of one monomer across the triple bond of another. In contrast, thermal and Zeigler polymerizations are considered to proceed by additions of an active chain-end across successive triple bonds in analogy to vinyl polymerisation of double bonds.

$RhCl(Ph_3P)_3$ polymerisation proceeds readily at 50—70° in bulk monomer without added co-catalyst. When the reaction is conducted at 0—20° with 0·016 mol./l. of rhenium for three days a 50% yield of *trans*-1,4-diphenylbutenyne crystallizes from a syrup of oligamers. Styrene fails to polymerise under the same conditions at either 0—20° or 50—70°.

The *trans*-1,4-diphenylbutenyne clearly indicates addition of PhC≡CH through its C–H bond across another acetylenic group. One may infer that the Rh complex assists in this process. The dissociative additions of H_2, HCl, and MeI to this complex are already known.[2] Similar addition of PhC≡CH (as PhC≡C– and –H) into the Rh co-ordination sphere could be followed by subsequent addition to another phenylacetylene unit π-complexed through its triple bond. Subsequent similar additions to terminal triple bonds will result in chain growth.



The addition polymerisation of alternating diene and dithiol units[3] represents an analogous system not employing transition-metal catalysis.

$$H_2C{=}C{-}C{=}CH_2 + HS\cdots SH \rightarrow [\cdots S{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}S\cdots]$$

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[1] R. J. Kern, *Polymer Preprints*, Amer. Chem. Soc. Meeting, San Francisco, April, 1968.
[2] J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1966, 1711.
[3] C. S. Marvel, *Rec. Chem. Prog.*, 1951, **12**, 185.