

Coupling Electrocatalysis (Electron Transfer Chain) with Organometallic Catalysis: Polymerisation of Terminal Alkynes Catalysed by $[\text{W}(\text{CO})_3(\text{NCMe})_3]$ and $[\text{Fe}(\text{cp})_2]^+\text{PF}_6^-$ (cp = η^5 -cyclopentadienyl)

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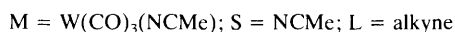
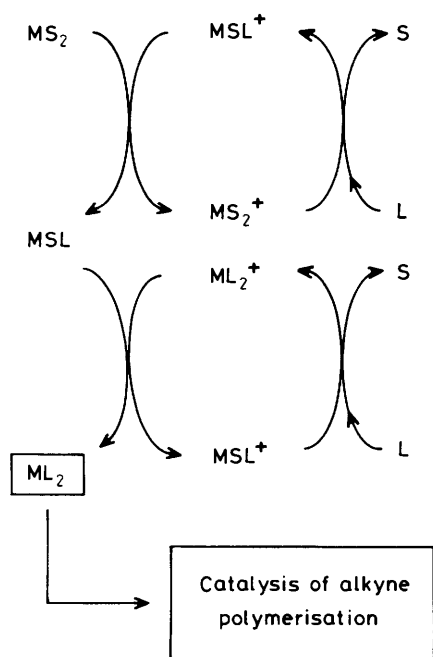
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Terminal alkynes (RC_2H ; R = Ph, Bu^n) are instantaneously polymerized at 20 °C by 1% of $\text{W}(\text{CO})_3(\text{NCMe})_3$ (**1**) and 0.01% of $[\text{Fe}(\text{cp})_2]^+\text{PF}_6^-$ (**2**) in a system which couples electrocatalysis (electron transfer chain) with organometallic catalysis (cp = η^5 -cyclopentadienyl).

Transition metal complexes with several labile ligands are finding increasing applications in catalysis. One way to stabilize ligands is to oxidize 18-electron complexes, so it is desirable to design complexes with several electron-releasing ligands, *i.e.* good σ donors which are not π acids, such as acetonitrile. Mono-electronic oxidation of $\text{W}(\text{CO})_3(\text{NCMe})_3$ (**1**)^{1a,b} is known to occur irreversibly at an easily accessible potential [$E^\circ = 0.2$ V vs. standard calomel electrode (S.C.E.)],^{1c} which induces decomplexation. The polymerization of terminal alkynes can be best catalysed by W complexes according to a well recognized 'methathesis-like' mechanism² which requires the stepwise co-ordination of two alkyne molecules. We then

reasoned that the irreversible oxidation of (**1**) could be effected with $[\text{Fe}(\text{cp})_2]^+\text{PF}_6^-$ (**2**),³ and in so doing generate an active, highly unsaturated W species able to co-ordinate two molecules of alkyne. With MeCN as the leaving ligand and alkyne as the incoming one, the electron transfer (E.T.) induced ligand exchange should be electrocatalytic with an exergonic cross E.T. step,⁴ because the alkyne is less electron releasing than MeCN. Such exchange of MeCN by PPh_3 in (**1**) is known.^{1c} In short, we are coupling organometallic catalysis with electrocatalysis.

Addition of 1% of (**1**)⁵ to a solution of phenylacetylene [in tetrahydrofuran (THF), MeCN, or toluene], slowly gave a

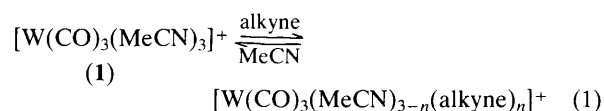


Scheme 1. Proposed mechanism for the coupling of electrocatalysis (ETC) and catalysis of alkyne polymerisation. For the sake of clarity, the initiation steps are not indicated. The initiators are cp_2Fe^+ (top cycle) and MSL^+ (bottom cycle).

substituted polyacetylene⁵ (*trans-cisoid* and *cis-transoid* in equal amounts based on i.r. data;^{5a} one week at 20 °C) with 12–15% yields, indicating turnover numbers of 12–15. The molecular weights of the polymer were around 15 000.† If, however, 0.1–0.2 equiv. of (2) per W complex was added, polymerization was very rapid and yields reached 40–45%

† The yields were measured for the materials obtained by dissolving the reaction products in CH_2Cl_2 , precipitating with MeOH, and drying *in vacuo*. Molecular weights were evaluated by gel permeation chromatography (g.p.c.) using a THF solution, a refractive index monitor and 2 × G MHXL and 1 × G 1000 HXL columns (reference: polystyrene).

(40–45 turnovers). When MeCN was the solvent the yield was not increased. Molecular weights were typically 25 000. The lack of catalyst efficiency with MeCN as the solvent is understandable, since the MeCN displaces the dissociation equilibrium in the wrong direction [equation (1)].



The maximum yields of polymers were obtained with 0.1–0.2 equiv. of (2) per W. When up to 1 equiv. of (2) per W was used, yields were reproducibly as low as 6% (only 3 turnovers). This indicates that the paramagnetic W species are not themselves catalytically active and that their role is in the E.T. processes, *i.e.* in the electrocatalytic cycle (electron transfer chain). Thus, the only role of (2) is to induce the electrocatalytic ligand exchange of MeCN by alkynes. Given this information and current knowledge of alkyne polymerization,² a tentative mechanism for the system proposed (Scheme 1).

We thank Dr. M. Birot (U.A. 35) for kindly recording g.p.c. data.

Received, 2nd November 1987; Com. 1588

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