

Metathesis Polymerization of Phenylacetylene by Arene Metal Tricarbonyl Complexes Promoted by Chloranil Acceptor

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Summary: Chloranil acceptor induces metathesis polymerization and block copolymerization of phenylacetylene by (arene)M(CO)₃ (arene = toluene, *o*-xylene, or mesitylene, M = Mo or W) complexes at ambient conditions. The mechanism of catalyst activation is one of thermal electron transfer, as suggested by spectral studies.

The past two decades have witnessed an increasing realization of the importance of odd-electron organometallic species in stoichiometric and catalytic transformations.¹ The observed large enhancement in the reaction rate upon oxidation or reduction of the respective 18-electron metal complexes and further amplification of this activation process are the basis for the now well-established electron-transfer-chain (ETC) catalysis that calls for, in principle, partial (*not stoichiometric*) oxidation of the metal complexes.² Metal-centered radicals, so generated in a chain-transfer mechanism, have been put to use in a variety of synthetically useful transformations, such as CO insertion, ligand substitution, and polymerization reactions.^{3–5} The conceptual similarities between such electrochemical (or chemical) and photochemical activation processes was pointed out by Vlcek⁶ who also suggested the possibility of photoinitiation of ETC catalysis for polymerization of acetylenes. We have been able to employ (arene)M(CO)₃ complexes (arene = toluene, *o*-xylene or mesitylene, M = Cr, Mo, or W) as catalysts for the polymerization of terminal alkynes like phenylacetylenes under thermal as well as ETC cata-

lytic conditions.⁷ But since our efforts in activating the (arene)M(CO)₃ complexes by photolysis for metathesis polymerization reactions turned futile, we sought for an alternate method of activation of the metal center by inducing charge transfer to an acceptor reagent. Herein, we report our findings in this novel form of activation of the soluble metal complexes by addition of chloranil for inducing metathesis polymerization of phenylacetylene.⁸

Addition of 1 equiv of chloranil to a solution containing an equimolar amount of the (toluene)Mo(CO)₃ complex and 50 equiv of the monomer, phenylacetylene (PA), induces rapid polymerization at ambient conditions to give a near quantitative yield of polyphenylacetylene (PPA), *vide* Scheme 1. The acceptor chloranil was chosen (Table 1) among many acceptors differing in their oxidation potentials but possessing similar structural characteristics.⁹

A systematic evaluation of the reactivity of (arene)M(CO)₃ complexes showed molybdenum-based complexes to be far superior to those of tungsten, while chromium complexes failed to initiate polymerization (Table 2). The poor reactivity of the chromium complexes could be attributed to the higher oxidation potential of the chromium catalyst compared to the molybdenum analogs.¹⁰ No appreciable difference in the yield of PPA was observed among the three arenes employed as the coordinating ligand, but coordinating solvents like CH₃-

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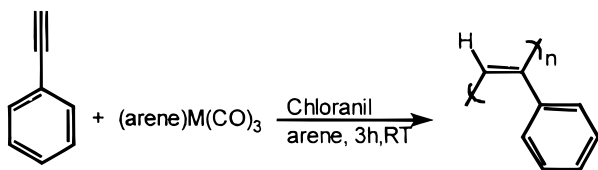
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Scheme 1. Metathesis Polymerization of (arene)M(CO)₃ Complexes Initiated by Chloranil



Arene = toluene, *o*-xylene or mesitylene. M = Mo or W.

Table 1. Effect of Acceptor on Yield of Polymer^a

acceptor	E_{red}°	ΔG°	% yield ^b
benzoquinone	-0.16	+0.455	0
2,6-dibromobenzoquinone	+0.18	+0.115	11
			35
-do- (at 50 °C)	+0.38	-0.085	94
chloranil	+0.85	-0.555	<5
DDQ			

^a Using the expression $\Delta G^{\circ} = E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) + C$, we have deduced the ΔG° for the electron transfer between the (mesitylene)Mo(CO)₃ complex and acceptors. The oxidation potential of the (mesitylene)Mo(CO)₃ complex is +0.295V vs SCE in DMF. ^b The yields of the polymer are based on the methanol-insoluble fraction.

Table 2. Effect of Catalyst on Polymer Yield

catalyst ^a	% yield ^b
(toluene)Mo(CO) ₃	90
(<i>o</i> -xylene)Mo(CO) ₃	92
(mesitylene)Mo(CO) ₃	96
(toluene)W(CO) ₃	0
(<i>o</i> -xylene)W(CO) ₃	70
(mesitylene)W(CO) ₃	33
(arene)Cr(CO) ₃	0
(CH ₃ CN) ₃ Mo(CO) ₃	7
(CH ₃ CN) ₃ W(CO) ₃	7

^a The acceptor was chloranil in an appropriate arene solvent. For (mesitylene)Mo(CO)₃, (mesitylene)W(CO)₃, (CH₃CN)₃Mo(CO)₃, and (CH₃CN)₃W(CO)₃, toluene was used as the solvent. ^b Yield of the methanol insoluble fraction.

CN inhibited polymerization,¹¹ implying ligation of the monomer to the metal as being crucial for chain propagation. However, deviation from ETC catalysis was observed when non-arene complexes in the presence of chloranil failed to initiate polymerization of PA, hinting at a different form of activation than that implied in the conventional ETC catalysis.⁵

The molecular weights of the polymers are fairly high ($M_n = 15\,000$ – $25\,000$; $\text{pdi} (M_w/M_n) = 1.6$ – 1.9) and are comparable with the results obtained with other known metathesis catalysts.¹² In addition, while thermal or ETC catalytic conditions⁷ yielded no block copolymer, (arene)Mo(CO)₃/chloranil catalyst was capable of generating living polymers to produce block copolymer of PA and norbornene (by ring-opening metathesis polymerization, ROMP) upon successive addition of the monomers. Both ¹H and ¹³C NMR spectra of the block copolymer obtained indicate the presence of blocks of polyphenylacetylene and ring-opened polynorbornene.¹³ Due to the broad aromatic signals from the PA unit, the signals from the olefinic protons do not resolve well from those of the aromatic protons and, hence, determination

(11) Various solvents were tried for the polymerization in this system. Solvent (% yield): toluene (90), chlorobenzene (35), CCl₄ (80), CHCl₃ (27), ether (12), THF (0), CH₃CN (0).

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of the percentage of ROMP product by comparison of the intensities of olefinic and aliphatic protons is rendered difficult.¹⁴ However, the IR spectrum of the block copolymer is devoid of any signal at 1298 cm^{-1} characteristic of the bridging CH₂ group in the C-7 position of the norbornene, in polynorbornene formed via vinylic addition route,¹⁵ giving credence to the hypothesis that polymerization in this system proceeds by metathesis.¹⁶ In addition, the GPC trace of the block copolymer shows a monomodal molecular weight distribution with $M_n = 7994$ and $\text{pdi} = 1.39$. The low pdi value also could suggest the living nature of the initiating catalytic systems.¹⁷

In order to delineate the mechanism of the polymerization reaction, the following spectral studies were undertaken. An UV spectrum of a solution of (toluene)Mo(CO)₃ complex and chloranil in an equimolar ratio showed no visible charge-transfer band, presumably due to the transient nature of the CT complex.¹⁸ Flow-cell FT-IR measurements¹⁹ indicated the disappearance of the band at 1693 cm^{-1} (ν_{CO} , chloranil) within 260 s from the start of the reaction. Concomitantly, a new band²⁰ at 1977 cm^{-1} appears at the expense of the bands due to the (toluene)Mo(CO)₃ complex at 1980 and 1904 cm^{-1} . Reduction of chloranil to the corresponding hydroquinone was suggested by the appearance of a band at 3504 cm^{-1} , and this was confirmed by isolating 2,3,5,6-tetrachloro-1,4-hydroquinone from the reaction mixture.²¹

Encouraging evidence for the electron-transfer process was obtained from the EPR and ⁹⁵Mo NMR studies. Addition of 1 equiv of chloranil to (toluene)Mo(CO)₃ solution in an aqueous cell placed inside the EPR cavity showed a strong signal at 3504 G (2.028 g), whereas the complex as such was EPR silent. The observed pattern of a strong central signal with five satellite peaks is suggestive of an oxidized molybdenum center.²² The intensity of this signal decreased with time and disappeared altogether after 35 min. Similarly, a solution of (toluene)Mo(CO)₃ complex in toluene showed an NMR

(13) ¹H and ¹³C NMR showed signals corresponding to both norbornene (NB) and phenylacetylene (PA) blocks. ¹H NMR (400 MHz, CDCl₃, PA and NB, δ , ppm): 1–3 (aliphatic, NB), 5–5.6 (olefinic, NB), 5.6–6.2 (olefinic, PA), 6.2–8 (phenyl, PA). ¹³C NMR (δ , ppm): 32.3, 32.9, 38.3, 41.3, 42.7, 43.3, 132.4, 133.1 (for NB) and 125–129 (br for PA). The ¹³C NMR of the polynorbornene block corresponds well to the documented spectral characteristics of a ring-opened polymer of norbornene with other conventional metathesis catalysts and has a high degree of trans content, for e.g., see: Ivin, K. J. *Olefin Metathesis*; Academic Press: London 1983; p 204.

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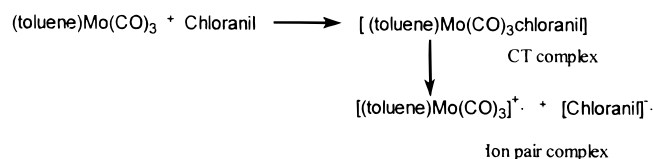
(18) A similar charge transfer induced aromatic deligation process between (HMB)₂Fe²⁺ and Mo(CO)₅⁻ has been reported (HMB = hexamethylbenzene). The authors proposed that CT occurs very fast and can be observed only at $-40\text{ }^{\circ}\text{C}$. Kochi, J. K.; Wei, C. H. *J. Organomet. Chem.* **1993**, *451*, 111.

(19) The reaction mixture was allowed to flow through an IR solution cell fitted with Teflon tubing. The cell was mounted in the IR instrument, and the spectrum was taken at various intervals of time.

(20) We are unable to assign this new band to any species.

(21) In a separate experiment, a toluene solution of (toluene)Mo(CO)₃ with 1 equiv of chloranil was kept in a refrigerator at $0\text{ }^{\circ}\text{C}$ for 1 week. White crystals were formed in the flask, which were isolated by filtration. The product was identified by various spectral methods and physical constants as 2,3,5,6-tetrachloro-1,4-hydroquinone, the reduced product of chloranil.

Scheme 2. Proposed Mode of Electron Transfer from the Complex to Chloranil



signal at $\delta -2030$ ppm due to the ^{95}Mo isotope,²³ with reference to the internal standard Na_2MoO_4 in D_2O . Upon addition of 1 equiv of chloranil with the monomer PA, a new signal at a downfield region of $\delta -1847$ ppm appeared and the parent signal decreased in intensity. It is suggested that depletion of electron density at the metal center is the reason for this observed large downfield shift for the new signal.

Collectively, the above data point to two key steps in the reaction, *viz.* electron-transfer and polymerization by metathesis. Apparently the formation of a transient CT complex between the $(\text{toluene})\text{Mo}(\text{CO})_3$ complex and the acceptor chloranil promotes a fast-electron-transfer process, generating a 17-electron $(\text{toluene})\text{Mo}(\text{CO})_3$ complex, an odd-electron species (Scheme 2). The formation of this complex is well-evidenced from the EPR and ^{95}Mo NMR spectral studies. This complex, which is substitution labile, would accommodate a molecule of terminal alkyne aided possibly by the ring-slipping of the arene ligand while initiation of polymerization by metathesis could be preceded by the now well-established η^2 -alkyne–vinylidene rearrangement route.²⁴ As the reaction proceeds rapidly even in electron-rich solvent, we suggest the mode of electron transfer between the complex to chloranil to be through the d orbital of the metal lying between the three carbonyl ligands and not through the arene ligand which is comparatively electron deficient by virtue of its coordination with the metal atom.²⁵

Experimental Section

All reactions were carried out under a purified nitrogen atmosphere. The solvents were distilled and dried by standard procedures and degassed by purging with nitrogen. All manipulations involving organometallic compounds were carried out in a glovebag or *via* syringes, in the case of liquids, by Schlenk techniques. Chloranil was purified by recrystallization.

The FT-IR measurements were done on a Perkin-Elmer FT-IR (model 1760). UV–vis spectral studies were done on

Perkin-Elmer (Lambda 17) spectrophotometer. UV spectra were taken in quartz cuvettes with a 1 cm path length. NMR spectra were recorded with a JEOL 400 MHz (model GSX 400) high-resolution NMR spectrometer in CDCl_3 with TMS as the internal standard. Chemical shifts were reported in ppm relative to the TMS signal. The molecular weights of the polymers were determined by Waters GPC, with RI detector (model 410). Analyses were performed using three ultra styragel columns (10^3 , 10^4 , and 10^5 Å) connected in series, maintained at 32 ± 1 °C with THF as the eluant at a flow rate of 1 mL per min. The molecular weight was determined with polystyrene as the calibration standard. Electron paramagnetic resonance spectra were recorded at room temperature on a Varian (model E112) X-band spectrometer using 100 KHz field modulation. The measurements were made in an aqueous cell with Teflon stoppers. Toluene was used as the solvent.

^{95}Mo NMR spectra were recorded at 25.9 MHz using the pulsed FT-NMR technique with a JEOL (GSX 400) 400 MHz NMR spectrometer. Molybdenum compounds with the natural abundance of ^{95}Mo (15.68%) were studied in the experiments. The spectra were obtained with cylindrical 10 mm NMR tubes. A 1 M solution of sodium molybdate (Na_2MoO_4) in D_2O was used as an internal standard, which was taken in a standard 5 mm NMR tube and sealed. The sealed tube was dipped inside the 10 mm NMR tube and the spectrum was taken. Chemical shift values were calculated in ppm with respect to the internal standard. The error in the measurements of the chemical shift values is ± 1 ppm. The following operating conditions were used for ^{95}Mo NMR measurements; sweep width, 40 000 Hz; accumulation time, 0.029 s; number of scans, 600–1200; 90° radio pulse at 15 μs . The data were accumulated with 32K data points in the time domain and were transformed with optimal exponential multiplication.

The complexes were obtained by refluxing the metal carbonyl in the respective arene for 6 h, followed by filtration and removal of the solvent in *vacuo*. The complexes were characterized by IR and NMR spectroscopy.

Typical Polymerization Procedure. Phenylacetylene (1.20 g, 10 mmol) was taken in a dry 50 mL flask fitted with a septum, flushed with nitrogen, and $(\text{toluene})\text{Mo}(\text{CO})_3$ (0.0557 g, 0.2 mmol) in 5 mL of toluene was added by syringe. Chloranil (0.0503 g, 2 mmol) dissolved in 15 mL of degassed toluene was added to the flask by syringe. The solution was stirred for 3 h at room temperature, maintained in a water bath. The brown-colored reaction mixture was poured into excess methanol, and the polymer was filtered *via* a crucible, washed with methanol, and dried in *vacuo* (yield 0.92 g, 90%).

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Supporting Information Available: ^1H NMR of PPA, IR and ^1H and ^{13}C NMR spectra of the block copolymer, PPA-PNBE, GPC trace of copolymer, PPA-PNBE, and EPR and ^{95}Mo NMR spectra for a $(\text{toluene})\text{Mo}(\text{CO})_3$ complex/chloranil mixture (7 pages). Ordering information is given in any current masthead page.

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