$M(CO)_6$ -RCl_n-hv catalysts (M = W, Mo; RCl_n = PhCCl₃, Ph₂CCl₂): new catalyst systems for the metathesis polymerization of substituted acetylenes and cycloalkenes

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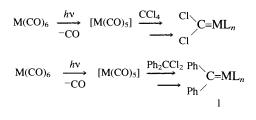
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The $M(CO)_6$ - RCl_n -hv systems (M = W, Mo; RCl_n = PhCCl₃, Ph₂CCl₂) work as effective catalysts for the polymerizations of substituted acetylenes and norbornene to provide high molecular weight polymers in good yields, where RCl_n are sufficient in catalytic amounts unlike CCl_4 .

We have found that the $M(CO)_6$ - CCl_4 - $h\nu$ catalyst systems (M = W and Mo) polymerize substituted acetylenes.^{1,2} It is known that these catalyst systems induce alkene metathesis as well.^{3,4} In these reactions, CCl₄ is used as solvent and works as a catalyst component at the same time. Metal carbenes are believed to be the active species of these reactions, which are generated as shown in Scheme 1.5,6 Further, the formation of 1 has been suggested in the reaction of the $W(CO)_6$ -Ph₂CCl₂-hv system with 2-ethoxynorbornene.⁵ It is, therefore, expected that the use of phenyltrichloromethane (PhCCl₃) and diphenyldichloromethane (Ph_2CCl_2) in place of CCl_4 in the $M(CO)_6$ -CCl₄-hv systems would lead to the formation of phenylcontaining metal carbenes via the process in Scheme 1 to effect the polymerization of substituted acetylenes and cycloalkenes. Herein we report that the $M(CO)_6 - RCl_n - hv$ systems (M = W, Mo; $RCl_n = PhCCl_3$, Ph_2CCl_2) serve as effective catalysts in the polymerization of various substituted acetylenes and norbornene (bicyclo[2.2.1]hept-2-ene) and that these organic chlorides are much more effective than CCl₄ as catalyst components.

A typical polymerization procedure is as follows: A toluene solution (5 cm³) of W(CO)₆ (0.10 mmol) and Ph₂CCl₂ (0.20 mmol) was irradiated with a 200 W high-pressure Hg lamp at 30 °C for 1 h. To this catalyst solution was added a toluene solution (5 cm³) of phenylacetylene (5.0 mmol). The polymerization was carried out in the dark at 30 °C for 24 h. All these processes were conducted under dry nitrogen.

The effect of the organic chloride concentrations on the polymerization of phenylacetylene was first examined. Eventually, the polymer yield showed maxima at PhCCl₃ = 100 mmol dm⁻³ and Ph₂CCl₂ = 20 mmol dm⁻³, while the numberaverage molecular weights (M_n) of the polymers were higher than 1 × 10⁴ at such concentrations of the organic chlorides (Table 1, lines 1 and 2). This indicates that these organic chlorides are, quite interestingly, effective in amounts relatively close to that of W(CO)₆. This gives a striking contrast to the



(M = W, Mo; L = CO, Cl) Scheme 1 Plausible initiation mechanisms

case of CCl₄ which is needed in much larger amounts and is usually employed as solvent simultaneously.¹ Hence, various solvents such as cyclohexane, chlorobenzene and anisole can be used for the present catalyst systems. For instance, the polymerization of phenylacetylene in cyclohexane gave polymers with M_n as high as 70 000–90 000.

Several substituted acetylenes other than phenylacetylene also produced polymers. Thus, (2-trimethylsilyl)phenylacetylene afforded a high molecular weight polymer in a good yield with $W(CO)_6$ -based catalysts, while (2-trifluoromethyl)-phenylacetylene and *tert*-butylacetylene gave similar results with $Mo(CO)_6$ -based catalysts (Table 1, lines 3–5). Therefore, the present catalyst systems prove to exhibit activities similar to those of the $M(CO)_6$ -CCl₄-hv counterparts.

Norbornene, a bicyclic alkene, also produced high molecular weight polymers ($M_n \ 1.0 \times 10^5 - 4.0 \times 10^5$) in the presence of $M(CO)_6$ -RCl_n-hv systems (Table 2). In particular, a combination of $Mo(CO)_6$ and PhCCl₃ achieved a high yield of polymer. To our knowledge, few examples have been reported regarding the polymerization of cycloalkenes by $M(CO)_6$ -hv catalyst systems.⁷

It is especially worth noting that 2 equiv. of Ph_2CCl_2 are sufficient for each $M(CO)_6$. This seems to imply that the formed metal diphenylcarbenes (M=CPh₂) are more stable than the metal dichlorocarbenes (M=CCl₂). The $M(CO)_6$ -CCl₄-hv systems become inhomogeneous after UV irradiation and the elucidation of the active species is difficult.⁸ The present

Table 1 Polymerization of substituted acetylenes by M(CO)₆-RCl_n-hv^a

		RCl _n	Polymer ^b		
Monomer	М		Yield (%)	$M_{\rm n}/10^{3}$ c	$M_{\rm w}/M_{\rm n}^c$
HC≡C-	W	PhCCl ₃	68	17	1.82
нс≡с-∕∕	W	Ph ₂ CCl ₂	70	16	1.88
Me ₃ Si HC≡C- CF ₃	W	Ph ₂ CCl ₂	55	82	2.80
HCEC	Мо	PhCCl ₃	64	390	1.56
HC≡CBu ^t	Мо	PhCCl ₃	99	900	2.11

^{*a*} Catalyst preparation: $M(CO)_6$ -RCl_n solution UV-irradiated at 30 °C for 1 h. Polymerization: in toluene, 30 °C, 24 h (dark); $[M]_0 = 0.50 \text{ mol } dm^{-3}$, $[M(CO)_6] = 10 \text{ mmol } dm^{-3}$, $[PhCCl_3] = 100 \text{ mmol } dm^{-3}$, $[Ph_2CCl_2] = 20 \text{ mmol } dm^{-3}$. ^{*b*} Methanol-insoluble product. ^{*c*} By GPC (polystyrene gel columns; eluent CHCl₃; RI detector; polystyrene calibration).

catalyst systems should generate metal carbenes having bulky phenyl group(s) but were also inhomogeneous. Further studies on the characteristics of the present catalyst systems are under way.

Table 2 Polymerization of norbornene by $M(CO)_6$ -RCl_n- $h\nu^a$

М	RCl _n	Conversion (%)	Polymer ^b			
			Yield (%)	$M_{\rm n}/10^{3c}$	$M_{\rm w}/M_{\rm n}^c$	
w	PhCCl ₃	47	47	180	2.06	
W	Ph_2CCl_2	7	7	130	2.71	
Mo	PhCCl ₃	80	66	170	2.35	
Mo	Ph ₂ CCl ₂	61	39	400	1.83	

^{*a*} Catalyst preparation: $M(CO)_6$ -RCl_n solution UV-irradiated at 30 °C for 1 h. Polymerization: in toluene, 30 °C, 24 h (dark); $[M]_0 = 0.50 \text{ mol dm}^{-3}$, $[M(CO)_6] = 10 \text{ mmol dm}^{-3}$, $[PhCCl_3] = 100 \text{ mmol dm}^{-3}$, $[Ph_2CCl_2] = 20 \text{ mmol dm}^{-3}$. ^{*b*} Methanol-insoluble product. ^{*c*} By GPC (polystyrene gel columns; eluent CHCl₃; RI detector; polystyrene calibration).

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