## $M(CO)_{6}-RCI_{n}-hv$  catalysts (M = W, Mo;  $RCI_{n}$  =  $PhCCI_{3}$ ,  $Ph_{2}CCI_{2}$ ): new **catalyst systems for the metathesis polymerization of substituted acetylenes and c ycloalkenes**

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The  $M(CO)_{6} - RCl_{n} - hv$  systems (M = W, Mo;  $RCl_{n}$  = PhCCl<sub>3</sub>, Ph<sub>2</sub>CCl<sub>2</sub>) work as effective catalysts for the **polymerizations of substituted acetylenes and norbornene to provide high molecular weight polymers in good yields, where RCl, are sufficient in catalytic amounts unlike CC14.** 

We have found that the  $M(CO)_6-CCl_4-hv$  catalyst systems (M  $=$  W and Mo) polymerize substituted acetylenes.<sup>1,2</sup> It is known that these catalyst systems induce alkene metathesis as well. $3,4$ In these reactions,  $CCl<sub>4</sub>$  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  $W(CO)_{6} - Ph_{2}CC1_{2} - hv$ system with 2-ethoxynorbornene.<sup>5</sup> It is, therefore, expected that the use of phenyltrichloromethane  $(PhCCI<sub>3</sub>)$  and diphenyldichloromethane (Ph<sub>2</sub>CCl<sub>2</sub>) in place of CCl<sub>4</sub> in the M(CO)<sub>6</sub>- $CCl_4-hv$  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)<sub>6</sub>-RCl<sub>n</sub>-hv systems (M = W, Mo;  $RCl_n$  = PhCCl<sub>3</sub>, Ph<sub>2</sub>CCl<sub>2</sub>) serve as effective catalysts in the polymerization of various substituted acetylenes and norbornene **(bicyclo[2.2.l]hept-2-ene)** and that these organic chlorides are much more effective than  $CCI<sub>4</sub>$  as catalyst components.

A typical polymerization procedure is as follows: A toluene solution (5 cm<sup>3</sup>) of  $W(CO)_{6}$  (0.10 mmol) and  $Ph_2CC1_{2}$  (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  $PhCCl<sub>3</sub> = 100$ mmol dm<sup>-3</sup> and Ph<sub>2</sub>CCl<sub>2</sub> = 20 mmol dm<sup>-3</sup>, while the numberaverage molecular weights  $(M_n)$  of the polymers were higher than  $1 \times 10^4$  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  $W(CO)<sub>6</sub>$ . This gives a striking contrast to the



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

case of CC14 which is needed in much larger amounts and is usually employed as solvent simultaneously.<sup>1</sup> 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-trimethylsily1)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  $Mo(CO)<sub>6</sub>$ -based catalysts (Table 1, lines 3–5). Therefore, the present catalyst systems prove to exhibit activities similar to those of the  $M(CO)_6-CCl_4-hv$  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  $M(\overrightarrow{CO})_6$ -RCl<sub>n</sub>-hv systems (Table 2). In particular, a combination of  $Mo(CO)_{6}$  and PhCCl<sub>3</sub> 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  $Ph<sub>2</sub>CCl<sub>2</sub>$  are sufficient for each  $M(CO)<sub>6</sub>$ . This seems to imply that the formed metal diphenylcarbenes  $(M=CPh<sub>2</sub>)$  are more stable than the metal dichlorocarbenes ( $M=CCl_2$ ). The  $M(CO)_6-CCl_4-hv$  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  $M(CO)_{6}-RCl_{n}-h\nu^{a}$ 

			Polymer <sup>b</sup>			
Monomer	M	RCl <sub>n</sub>	Yield $(\%)$	$M_{\rm n}$ /10 <sup>3</sup> c	$M_{\rm w}/M_{\rm n}$	
$HC \equiv C$	W	PhCCl <sub>3</sub>	68	17	1.82	
$HC = C$	W	Ph <sub>2</sub> CCl <sub>2</sub>	70	16	1.88	
Me <sub>3</sub> Si $HC \equiv C$ CF <sub>3</sub>	W	Ph <sub>2</sub> CCl <sub>2</sub>	55	82	2.80	
$HC = C$	Mo	PhCCl <sub>3</sub>	64	390	1.56	
HC⊟CBu <sup>t</sup>	Mo	PhCCl <sub>3</sub>	99	900	2.11	

*a* Catalyst preparation: M(CO)<sub>6</sub>-RCl<sub>n</sub> solution UV-irradiated at 30 °C for 1 h. Polymerization: in toluene,  $30^{\circ}$ C, 24 h (dark); [M]<sub>0</sub> = 0.50 mol dm<sup>-3</sup>,  $[M(CO)_6] = 10$  mmol dm<sup>-3</sup>,  $[PhCCl_3] = 100$  mmol dm<sup>-3</sup>,  $[Ph_2CCl_2] = 20$ mmol dm-3. *h* Methanol-insoluble product. *c* By GPC (polystyrene gel columns; eluent CHC13; **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  $M(CO)_{6}-RCl_{n}-hv^{a}$ 

м		Conversion (%)	Polymer <sup>b</sup>			
	RCI,		Yield $(\%)$	$M_{\rm n}$ /10 <sup>3c</sup>	$M_{\rm w}/M_{\rm g}c$	
W	PhCCl <sub>3</sub>	47	47	180	2.06	
W	$Ph2$ CCl <sub>2</sub>			130	2.71	
Mo	PhCCl <sub>3</sub>	80	66	170	2.35	
Mo	Ph <sub>2</sub> CCl <sub>2</sub>	61	39	400	1.83	

*<sup>a</sup>*Catalyst preparation: M(C0)6-RC1, solution UV-irradiated **at** 30 "C for 1 h. Polymerization: in toluene, 30 °C, 24 h (dark);  $[M]_0 = 0.50$  mol dm<sup>-3</sup>,  $[M(CO)_6] = 10$  mmol dm<sup>-3</sup>,  $[PhCCl_3] = 100$  mmol dm<sup>-3</sup>,  $[Ph_2CCl_2] = 20$ mmol dm<sup>-3</sup>. *b* Methanol-insoluble product. <sup>c</sup> By GPC (polystyrene gel columns; eluent CHCl<sub>3</sub>; RI detector; polystyrene calibration).

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