Novel Group 6 Transition Metal Catalysts, MCl$_2$(CO)$_3$(AsPh$_3$)$_2$ (M = W, Mo), for the Metathesis Polymerization of Substituted Acetylenes

Hideo Nakako, Yoshihiko Misumi, Toshio Masuda,[†]
Lajos Bencze,* and Gabor Szalai*

Department of Polymer Chemistry, Kyoto University, Kyoto 606–8501, Japan
**Department of Organic Chemistry, University of Veszprém,*
P.O. Box 158, Veszprém H-820, Hungary

ABSTRACT: It was examined whether group 6 transition metal complexes, MCl$_2$(CO)$_3$(AsPh$_3$)$_2$ (M = W, Mo), work as catalysts in the polymerization of substituted acetylenes. WCl$_2$(CO)$_3$(AsPh$_3$)$_2$ polymerized phenylacetylene and its ring-substituted derivatives in good yields, while MoCl$_2$(CO)$_3$(AsPh$_3$)$_2$ polymerized 1-chloro-1-octyne, *tert*-butylacetylene, and ortho-substituted phenylacetylenes in high yields. These complexes worked as catalysts alone and did not require either of ultra violet (UV) irradiation and CCl$_4$ solvent unlike the M(CO)$_6$–CCl$_4$–hν systems. Consequently, various solvents including toluene and cyclohexane were available. Addition of Lewis acids and organometallics did not enhance the catalytic activity of these complexes. The present catalysts are relatively stable to air and moisture, and hence convenient and versatile in the polymerization of various acetylenes.
KEY WORDS Tungsten Carbonyl Complex / Molybdenum Carbonyl Complex / Transition Metal Catalyst / Metathesis Polymerization / Substituted Acetylene / Substituted Polyacetylene /

A variety of transition metal catalysts induce the polymerization of substituted acetylenes.[1,2] Among them are group 6 transition metal (Mo, W) catalysts, which are roughly classified into metal chloride-based catalysts,[3] metal hexacarbonyl-based catalysts,[4,5] other metal carbonyl-based catalysts,[6,7] Fischer-type metal carbene catalysts,[8,9] Schrock-type metal carbene catalysts,[10–12] etc. Metal chloride-based catalysts are usually employed in conjunction with organometallic cocatalysts and characterized by their high activity. The M(CO)$_6$–CCl$_4$–hν systems, which are typical metal hexacarbonyl-based catalysts, generate active species when M(CO)$_6$ is ultra violet (UV) irradiated in CCl$_4$ solution. Metal carbene catalysts have structures identical or close to those of the propagating species, and hence may work as living polymerization catalysts. In contrast, polymerizations by metal complexes having carbonyl and other ligands are rather rare, and their detailed behavior and mechanism remain unknown.

Bencze and coworkers have reported that group 6 transition metal complexes, MCl$_2$(CO)$_3$(PPh$_3$)$_2$ (M = W, Mo), are effective in olefin metathesis and further that MCl$_2$(CO)$_3$(AsPh$_3$)$_2$ (M = W, Mo) induce ring-opening metathesis polymerization (ROMP) of norbornene.[13] These complexes exhibit catalytic activity for themselves, *i.e.*, in the absence of a chlorinated hydrocarbon and without UV irradiation. Further, it has been revealed that various MX$_2$(CO)$_3$L$_2$ (M = W, Mo; X = Cl, Br, I; L = PPh$_3$, AsPh$_3$, SbPh$_3$) complexes effect ROMP.[14] These catalysts are expected to be applicable to metathesis polymerizations of substituted acetylenes, because the propagating species in the polymerization of substituted acetylenes are also metal carbenes.

In the present study, we investigated the polymerization of substituted acetylenes by MCl$_2$(CO)$_3$(AsPh$_3$)$_2$ (M = W, Mo) to clarify (i) the effectiveness of MCl$_2$-(CO)$_3$(AsPh$_3$)$_2$ (M = W, Mo) as polymerization cata-

lysts, and (ii) the influences of reaction conditions on the polymerization.

EXPERIMENTAL

Materials

MCl$_2$(CO)$_3$(AsPh$_3$)$_2$ (M = Mo or W) complexes were prepared by chlorination of the corresponding M(CO)$_6$ complexes and the subsequent reaction of the resulting MCl$_2$(CO)$_4$ intermediates with AsPh$_3$ in acetone, as described in the literature.[15] Phenylacetylene (Aldrich), 1-decyne (Aldrich), 1-ethynylcyclohexene (Aldrich), and 1-phenyl-1-propyne (Aldrich) were distilled from calcium hydride. *p*-Methylphenylacetylene,[16,17] *m*-trifluoromethylphenylacetylene,[16,17] *o*-trifluoromethylphenylacetylene,[16,17] *o*-trimethylsilylphenylacetylene,[18,19] *tert*-butylacetylene,[20,21] and 1-chloro-1-octyne[22] were prepared according to literature method, and distilled from calcium hydride. Polymerization solvents were purified by the standard methods. Lewis acids (SnCl$_4$, AlBr$_3$, and ZrCl$_4$) and organometallic compounds (EtAlCl$_2$, *n*-Bu$_4$Sn, Et$_3$Al, and Et$_2$Zn) were commercially obtained and used without purification.

Procedures

Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen. UV irradiation was carried out with a 200-W high-pressure mercury lamp from a distance of 5 cm at 60°C for 1 h. The monomer conversions were determined by gas chromatography using bromobenzene as internal standard. The resulting polymers were isolated by precipitation in a large amount of methanol and dried at reduced pressure. Number- and weight-average molecular weights (M_n and M_w, respectively) of the polymers were determined by gel permeation chromatography (eluent, chloroform; Shodex columns K804, K805 and K806; polystyrene calibration).

[†] To whom correspondence should be addressed.

Table I. Polymerization of substituted acetylenes by $MCl_2(CO)_3(AsPh_3)_2$ (M = W, Mo)[a]

Monomer	$WCl_2(CO)_3(AsPh_3)_2$		$MoCl_2(CO)_3(AsPh_3)_2$	
	Yield/%	$M_n \times 10^{-3}$	Yield/%	$M_n \times 10^{-3}$
HC≡C-⟨◯⟩	66	33.0	3	—
HC≡C-⟨◯⟩-CH₃	72	35.2	0	—
HC≡C-⟨◯⟩ CF₃	45	27.4	0	—
HC≡C-⟨◯⟩ F₃C	98	391	98	276
HC≡C-⟨◯⟩ Me₃Si	100	440	100	439
HC≡C-t-Bu[b]	24	42.5	92	335
HC≡C-n-C₈H₁₇	13	—	0	—
HC≡C-⟨◯⟩	22	Insoluble	0	—
CH₃C≡C-⟨◯⟩	0	—	0	—
ClC≡C-n-C₆H₁₃	0	—	50	226

[a] Polymerized in toluene at 60°C for 24 h; $[MCl_2(CO)_3(AsPh_3)_2]$, 2.0 mM; $[M]_0$, 0.50 M: the yield and M_n are for the methanol-insoluble product. [b] Polymerized at 40°C.

RESULTS AND DISCUSSION

Polymerization of Various Substituted Acetylenes

It was examined what substituted acetylenes can be polymerized by the present catalysts (Table I). The $WCl_2(CO)_3(AsPh_3)_2$ complex polymerized phenylacetylene and its p-Me, m-CF₃, o-CF₃, and p-Me₃Si derivatives to give polymers in high yields. The phenylacetylenes with bulky ortho-substituents provided very high molecular weight polymers ($M_n = 380000$—440000). Although tert-butylacetylene, 1-decyne, and 1-ethynylcyclohexene were consumed, the polymer yields were rather low. Disubstituted acetylenes such as 1-phenyl-1-propyne and 1-chloro-1-octyne did not polymerize with this complex. When $MoCl_2(CO)_3(AsPh_3)_2$ was used as catalyst, o-CF₃- and o-Me₃Si-phenylacetylenes, 1-chloro-1-octyne, and tert-butylacetylene polymerized in high yields; the molecular weights of the polymers reached 200000—300000. On the other hand, phenylacetylenes without bulky ortho-substituents hardly polymerized.

The relationship between the catalysts and the monomers is similar to those so far observed for other W and Mo catalysts,[4] and one can see that the central atom of the catalyst has a strong influence on the monomer reactivity. The polydispersity ratios (M_w/M_n) of all the formed polymers were 1.3—2.0. On the basis of the above-stated results, we further investigated the polymerization of phenylacetylene by $WCl_2(CO)_3(AsPh_3)_2$ and that of 1-chloro-1-octyne by $MoCl_2(CO)_3(AsPh_3)_2$ in detail. Phenylacetylene, commercially readily available monomer, was used in the $WCl_2(CO)_3(AsPh_3)_2$-catalyzed polymerization, while 1-chloro-1-octyne was

employed for $MoCl_2(CO)_3(AsPh_3)_2$ because phenylacetylene hardly polymerized with this catalyst.

Effects of Halogen-Containing Solvents and UV Irradiation

Both a halogen-containing solvent and UV irradiation are necessary in the conventional metal hexacarbonyl-based catalyst systems. Their effects were investigated in the present catalyst systems (Table II).

The polymerization of phenylacetylene by $WCl_2(CO)_3(AsPh_3)_2$ proceeded in toluene without UV irradiation to give a red polymer with M_n 33000 in a 66% yield. Even though the catalyst solution was UV irradiated, the catalyst activity did not change. The catalyst exhibited in CCl_4 an activity similar to that in toluene. The polymerization of 1-chloro-1-octyne by $MoCl_2(CO)_3(AsPh_3)_2$ also proceeded in toluene to yield a white polymer with M_n 240000 in a 50% yield. Again, use of CCl_4 as solvent hardly affected the polymerization. However, UV irradiation deactivated this catalyst, probably because of the decomposition of the Mo complex. These results show that the polymerization of substituted acetylenes by the present catalysts proceeds in toluene without UV irradiation as in the case of norbornene. This gives a contrast to the polymerization by metal hexacarbonyl-based catalysts, which require both UV irradiation and CCl_4 solvent to generate the propagating species.

Effects of Various Solvents

Since CCl_4 solvent proved to be unnecessary in the present polymerization, other solvents might be available. Thus, various solvents were examined as polymerization solvents (Table III).

When aromatic solvents such as toluene, anisole, and bromobenzene were used in the polymerization of phenylacetylene by $WCl_2(CO)_3(AsPh_3)_2$, polymers with M_n 10000—30000 were obtained in good yields (30—70%). Cyclohexane and CCl_4 were also useful as polymerization solvents. On the other hand, n-hexane, which sparingly dissolves the catalyst and the polymer, polar $CHCl_3$, and basic cyclic ethers were less favorable. In the polymerization of 1-chloro-1-octyne by $MoCl_2(CO)_3(AsPh_3)_2$, the polymers were obtained in toluene, bromobenzene, and CCl_4, in good to moderate yields. The polymers had high molecular weights of ca. 14×10^4—23×10^4. Polymer was hardly or not at all obtained in other solvents examined.

Effects of Additives

It is known that Lewis acids and organometallic compounds activate metal carbonyl-based catalysts[23] and metal chloride-based catalysts,[24] respectively. Thus, the effects of Lewis acids and organometallic compounds on the present polymerizations were investigated (Table IV). The additives were used in an equivalent amount to the catalysts.

In the polymerizations of phenylacetylene by $WCl_2(CO)_3(AsPh_3)_2$, the polymer yields were similar to or lower than that by the catalyst alone (67—3%), when Lewis acids such as $SnCl_4$, $AlBr_3$, $ZrCl_4$, and $EtAlCl_2$ were added. Organometallic compounds such as n-Bu₄Sn, Et₃Al, and Et₂Zn did not give positive effects,

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Table II. Effects of solvents and UV irradiation on the polymerization of substituted
acetylenes by $MCl_2(CO)_3(AsPh_3)_2$ (M = W, Mo)[a]

Solvent	Irradn time/h	HC≡CPh/W			ClC≡C-n-C_6H_{13}/Mo		
		Monomer convn/%	Yield/%	$M_n \times 10^{-3}$	Monomer convn/%	Yield/%	$M_n \times 10^{-3}$
Toluene	0	85	66	33.0	52	50	226
Toluene	1	84	65	34.0	37	32	204
CCl_4	0	98	82	12.0	25	23	209
CCl_4	1	99	72	14.0	9	7	132

[a] Polymerized at 60°C for 24 h; $[MCl_2(CO)_3(AsPh_3)_2]$, 2.0 mM; $[M]_0$, 0.50 M: the yield and M_n are for the methanol-insoluble product.

Table III. Effect of various solvents on the polymerization
of substituted acetylenes by $MCl_2(CO)_3(AsPh_3)_2$
(M = W, Mo)[a]

Solvent	HC≡CPh/W		ClC≡C-n-C_6H_{13}/Mo	
	Yield/%	$M_n \times 10^{-3}$	Yield/%	$M_n \times 10^{-3}$
Toluene	66	33.0	50	226
Anisole	34	10.2	4	92.0
PhBr	35	10.0	18	140
Cyclohexane	64	37.2	3	120
CCl_4	82	12.0	23	210
n-Hexane	1	21.0	0	—
$CHCl_3$	20	3.60	0	—
THF	26	7.00	0	—
Dioxane	10	6.00	0	—

[a] Polymerized at 60°C for 24 h; $[MCl_2(CO)_3(AsPh_3)_2]$, 2.0 mM; $[M]_0$, 0.50 M: the yield and M_n are for the methanol-insoluble product.

Table IV. Effect of various additives on the polymerization
of substitute acetylenes by
$MCl_2(CO)_3(AsPh_3)_2$ (M = W, Mo)[a]

Additive	HC≡CPh/W		ClC≡C-n-C_6H_{13}/Mo	
	Yield/%	$M_n \times 10^{-3}$	Yield/%	$M_n \times 10^{-3}$
None	66	33.0	50	226
$SnCl_4$	60	21.0	17	165
$AlBr_3$	9	8.40	15	110
$ZrCl_4$	67	28.3	18	160
$EtAlCl_2$	3	30.0	29	196
n-Bu_4Sn	65	40.0	38	224
Et_3Al	32	26.0	42	292
Et_2Zn	31	38.5	11	69.0

[a] Polymerized in toluene, at 60°C for 24 h; $[MCl_2(CO)_3(AsPh_3)_2]$, 2.0 mM; [Additive], 2.0 mM; $[M]_0$, 0.50 M: the yield and M_n are for the methanol-insoluble product.

(a) HC≡CPh / $WCl_2(CO)_3(AsPh_3)_2$

(b) ClC≡C-n-C_6H_{13} / $MoCl_2(CO)_3(AsPh_3)_2$

Figure 1. Effect of temperature on the polymerization of substituted acetylenes by $MCl_2(CO)_3(AsPh_3)_2$ (M = W, Mo) (in toluene, 24 h; $[MCl_2(CO)_3(AsPh_3)_2] = 2.0$ mM; $[M]_0 = 0.50$ M).

either; *i.e.*, the polymer yields were 65—31%, and were not higher than that with the catalyst alone (66%). A similar tendency was observed also in the polymerizations of 1-chloro-1-octyne by $MoCl_2(CO)_3(AsPh_3)_2$. Hence it is assumed that the initiation reaction and/or the properties of propagating species in the present polymerization differ from those for metal chloride- and metal carbonyl-based catalyst systems.

Temperature Dependence

The effect of polymerization temperature was investigated (Figure 1). Polymerization of phenylacetylene by $WCl_2(CO)_3(AsPh_3)_2$ hardly proceeded at low temperatures of 0—20°C, and the monomer conversions after 24 h were no more than 10—20%. However, with ele-
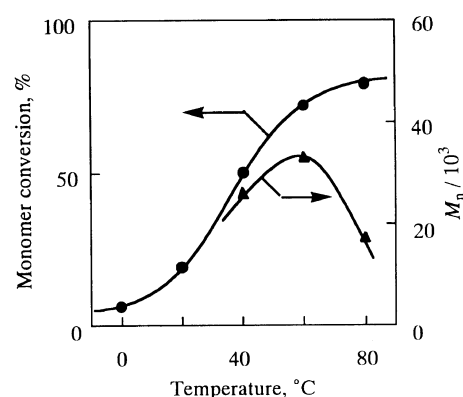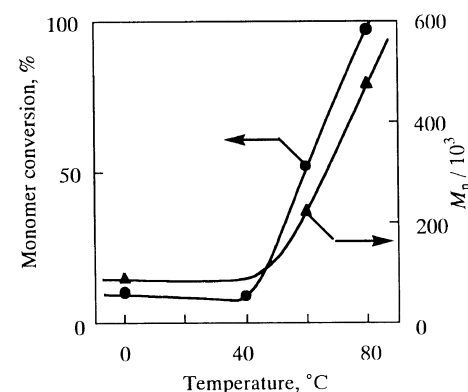
vating temperature to 60 and 80°C, the monomer conversions increased up to 70—80%, and the M_n values reached 20000—30000. The polymerization of 1-chloro-1-octyne by $MoCl_2(CO)_3(AsPh_3)_2$ hardly proceeded at 0 and 40°C. This polymerization gave the most favorable result at 80°C, *i.e.*, produced a polymer of M_n ca. 5×10^4 virtually quantitatively. These results indicate that the activities of these catalysts are lower than that of the metal chloride-based catalysts and similar to those of the metal carbonyl-based catalysts.[1,2]

Effect of Monomer Concentration

Figure 2 shows the effect of monomer concentration. In the polymerization of phenylacetylene by $WCl_2(CO)_3$-$(AsPh_3)_2$, the monomer conversion slightly decreased with increasing monomer concentration, whereas it

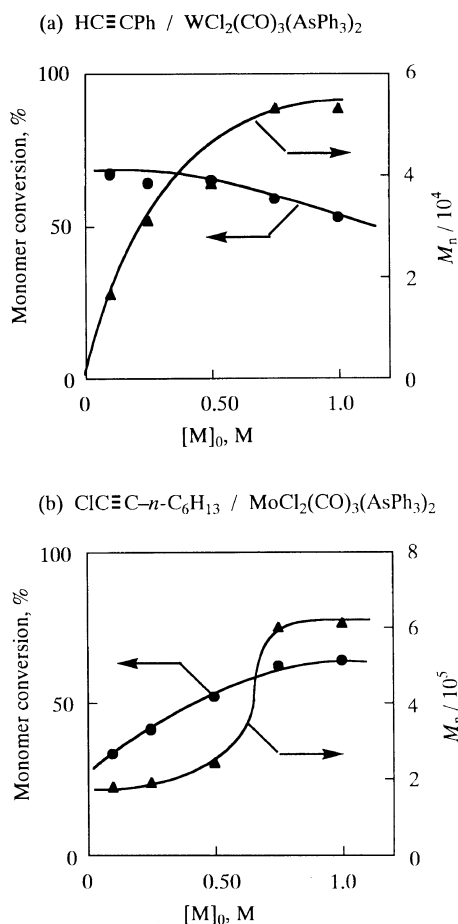(a) HC≡CPh / $WCl_2(CO)_3(AsPh_3)_2$

(b) ClC≡C-n-C_6H_{13} / $MoCl_2(CO)_3(AsPh_3)_2$

Figure 2. Effect of monomer concentration on the polymerization of substituted acetylenes by $MCl_2(CO)_3(AsPh_3)_2$ (M = W, Mo) (in toluene, 60°C, 24 h; $[MCl_2(CO)_3(AsPh_3)_2] = 2.0$ mM).

(a) HC≡CPh / $WCl_2(CO)_3(AsPh_3)_2$

(b) ClC≡C-n-C_6H_{13} / $MoCl_2(CO)_3(AsPh_3)_2$

Figure 3. Time profiles of the polymerization of substituted acetylenes by $MCl_2(CO)_3(AsPh_3)_2$ (M = W, Mo) (in toluene, 60°C; $[MCl_2(CO)_3(AsPh_3)_2] = 2.0$ mM; $[M]_0 = 0.50$ M).

increased to some extent in the polymerizations by $MoCl_2(CO)_3(AsPh_3)_2$. However, the influence of monomer concentration on conversion was rather small in both cases. The molecular weight of polymer increased with monomer concentration in both polymerizations; the molecular weights reached 53000 and 610000 in the polymerizations of phenylacetylene and 1-chloro-1-octyne, respectively.

Time Profile

Figure 3 shows time profiles of the polymerizations. Both polymerizations proceeded without an induction phase and leveled off at late stages. The molecular weight of polymer tended to increase with increasing monomer conversion in both cases.

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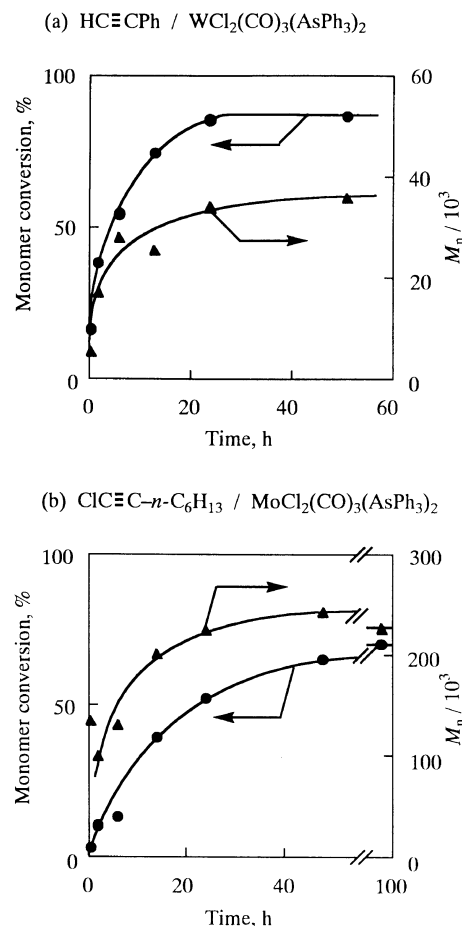4. T. Szymanska-Buzar, *J. Mol. Catal.*, 48, 43 (1988).
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