Composition vs catalytic properties of $M(CO)_3X_2L_2$ (M = Mo or W; X = Cl, Br or I; L = PPh_3, $AsPh_3$ or $SbPh_3$) initiators in romp of norbornene

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Abstract

Catalytic properties of 18 air stable $M(CO)_3X_2L_2$ (M = Mo or W; X = Cl, Br or I; L = PPh_3, $AsPh_3$ or $SbPh_3$) one-component initiators were screened in ring-opening metathesis polymerisation (ROMP) of norbornene. The rate of the polymerization, (V_p), varied between 7.8–32.9 $mol\,dm^{-3}\,h^{-1}$ in the case of the *tungsten* containing initiators, with I/PPh_3 and $Br/AsPh_3$ ligand combinations representing the two extremes respectively. The *cis*/*trans* double bonds form at about equal probability ($\sigma_c = 0.52$). The presence of L = $AsPh_3$ as a ligand seems to favour higher activity, higher *cis* selectivity and moderate blockiness. The higher *cis* selectivity of the tungsten complexes ($\sigma_c = 0.56$–0.58) induced by the I ligand is associated with significantly diminished activity. The activity of the more trans directing ($\sigma_c = 0.38$) *molybdenum* catalysts was about two orders of magnitude smaller ($V_p = 0.003$–2.50 $mol\,dm^{-3}\,h^{-1}$) increasing in the order, L = PPh_3, $AsPh_3$, $SbPh_3$, while the *cis* content and the blockiness of the polymer follow a reverse tendency.

Keywords: Tungsten-carbonyl-halides; Molybdenum-carbonyl-halides; ROMP; Olefin metathesis; Norbornene; Catalysis; Selectivity; Activity

1. Introduction

Thermally activated $W(CO)_3Cl_2L_2$ (L = PPh_3, $AsPh_3$) are known as unicomponent initiators in the ring-opening metathesis polymerization (ROMP) of strained cycloolefins (norbornene and norbornadiene) and their cross-metathesis with linear alkenes in bulk or in solution [1]. These catalysts deserve more attention for several reasons:
1. The initiator complexes are air stable;

2. They are readily available and widely variable;
3. The solutions of the living carbene catalyst are easily generated without the application of any organometallic cocatalysts;
4. The catalyst may be stored and applied as a stock solution;
5. The catalyst is rather tolerant to air and protic agents;
6. The activity may be enhanced by the addition of inorganic Lewis acids;
7. The metathesis reactions may quenched with organic carbonyl compounds.

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The aim of this work is to study systematically the change in the catalytic properties of the various metal complexes in the model ROMP of norbornene reaction as a function of the central metal atom, the halides and the donor ligands within the general initiator $M(CO)_3X_2L_2$.

2. Experimental

$M(CO)_3X_2L_2$ (M = Mo or W; X = Cl, Br or I; L = PPh_3, $AsPh_3$ or $SbPh_3$) complexes were prepared by halogenation of the corresponding $M(CO)_6$ complexes and the subsequent substitution of the resulting $M(CO)_4X_2$ intermediates in acetone solution by L as described by Colton [2–7] and Backer et al. [8,9]. The complexes

used for initiation were identified by their IR spectra (Table 1).

All experiments were conducted under deoxygenated argon. Benzene and norbornene were distilled from sodium/benzophenone before use.

ROMP experiments were carried out in a reaction mixture composed of benzene, norbornene (0.2 $mol\,dm^{-3}$) and $M(CO)_3X_2L_2$ (NBE/W 100 ± 3). The reaction mixture was immersed in an oil bath heated to 80°C and stirred by a magnetic stirrer. The reaction was quenched by the addition of ethanol when gelation became apparent or continued until acceptable quantity of product formed. The polymer was precipitated, washed in ethanol, dried and weighed. Yield (%) is defined by comparing the polymer weight to the weight of the norbornene

Table 1
Carbonyl stretching frequencies (ν_{CO}) at $M(CO)_3X_2L_2$ complexes

Complex	Medium	ν_{CO} (cm^{-1})			$\bar{\nu}_{CO}$(cm^{-1})
$W(CO)_3(PPh_3)_2Cl_2$	CH_2Cl_2	2023	1944	1909	1959
$W(CO)_3(AsPh_3)_2Cl_2$	CH_2Cl_2	2024	1946	1910	1960
$W(CO)_3(SbPh_3)_2Cl_2$	CH_2Cl_2	2020	1943	1907	1957
$W(CO)_3(PPh_3)_2Br_2$	CH_2Cl_2	2022	1946	1912	1960
	nujol	2011	1936	1897	1948
$W(CO)_3(AsPh_3)_2Br_2$	CH_2Cl_2	2033	1950	1911	1965
	nujol	2013	1938	1900	1950
$W(CO)_3(SbPh_3)_2Br_2$	CH_2Cl_2	2019	1945	1911	1958
	nujol	2010	1938	1902	1950
$W(CO)_3(PPh_3)_2I_2$	CH_2Cl_2	2016	1943	1926	1962
$W(CO)_3(AsPh_3)_2I_2$	CH_2Cl_2	2017	1943	1914	1958
	$CHCl_3$	2018	1943	1910	1957
$W(CO)_3(SbPh_3)_2I_2$	CH_2Cl_2	2017	1945	1912	1958
	$CHCl_3$	2018	1943	1910	1957
$Mo(CO)_3(PPh_3)_2Cl_2$	CH_2Cl_2	2022	1954	1904	1960
$Mo(CO)_3(AsPh_3)_2Cl_2$	CH_2Cl_2	2032	1965	1921	1973
$Mo(CO)_3(SbPh_3)_2Cl_2$	nujol	2018	1952	1907	1959
$Mo(CO)_3(PPh_3)_2Br_2$	CH_2Cl_2	2029	1963	1922	1971
	nujol	2018	1952	1908	1959
$Mo(CO)_3(AsPh_3)_2Br_2$	CH_2Cl_2	2029	1966	1926	1974
	nujol	2020	1956	1912	1963
$Mo(CO)_3(SbPh_3)_2Br_2$	CH_2Cl_2	2028	1962	1921	1970
	nujol	2017	1954	1911	1961
$Mo(CO)_3(PPh_3)_2I_2$	CH_2Cl_2	2015	1944	1903	1954
$Mo(CO)_3(AsPh_3)_2I_2$	CH_2Cl_2	2024	1963	1927	1971
$Mo(CO)_3(SbPh_3)_2I_2$	CH_2Cl_2	2024	1960	1922	1969
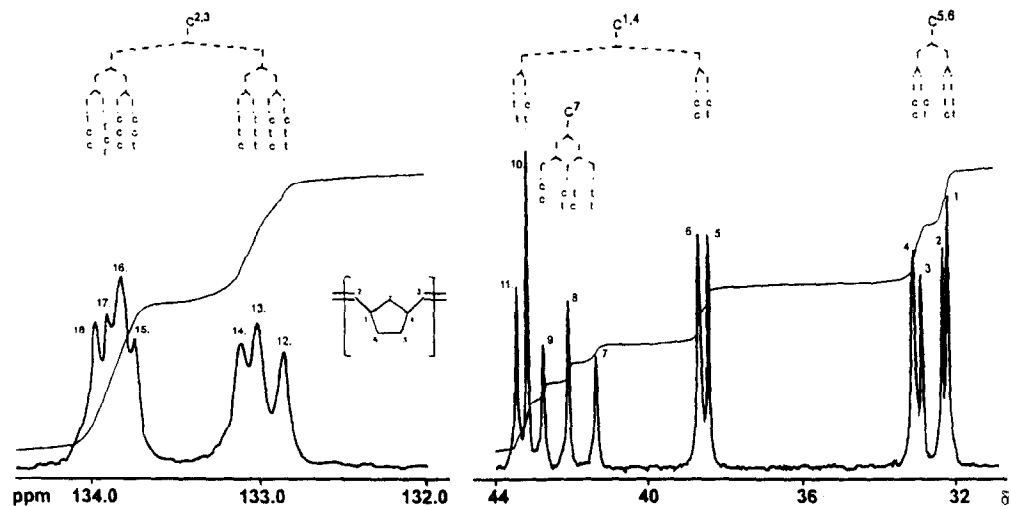
Fig. 1. Assignment of the ^{13}C NMR chemical shifts.

used. Reproducibility was tested in three independent runs using $W(CO)_3Cl_2(AsPh_3)_2$ catalyst. The yields varied within ±0.5%. An 'average reaction rate' (V_p, mol dm^{-3} h^{-1}) for the comparison of the different initiators is defined.

^{13}C{^{1}H} NMR spectra of the polymers were recorded in CDCl$_3$ solution at 125 MHz using a GE, GN Omega500 spectrometer. The assignments of ^{13}C NMR shifts based on previous analysis [10–13] were made as shown in Fig. 1. The microstructural details of the polymers were calculated from the NMR integrals [10–13].

Table 2
Yield, reaction rate and stereochemical data of polymers made by ROMP of norbornene using $M(CO)_3X_2L_2$/NBE/benzene systems

Precursor	y	V_r	σ_c	r_c	r_t	$r_c r_t$
$W(CO)_3(PPh_3)_2Cl_2$	38	21.1	0.42	1.30	2.82	3.67
$W(CO)_3(AsPh_3)_2Cl_2$	58	32.9	0.55	2.06	1.75	3.23
$W(CO)_3(SbPh_3)_2Cl_2$	49	27.2	0.51	1.82	1.85	3.37
$W(CO)_3(PPh_3)_2Br_2$	58	32.9	0.40	1.46	3.21	4.87
$W(CO)_3(AsPh_3)_2Br_2$	56	31.1	0.56	2.07	1.31	2.71
$W(CO)_3(SbPh_3)_2Br_2$	47	26.1	0.53	2.01	1.73	3.48
$W(CO)_3(PPh_3)_2I_2$	14	7.8	0.56	2.62	2.12	5.55
$W(CO)_3(AsPh_3)_2I_2$	34	18.9	0.58	2.37	1.85	4.38
$W(CO)_3(SbPh_3)_2I_2$	19	10.6	0.56	2.07	1.29	2.67
$Mo(CO)_3(PPh_3)_2Cl_2$	63 [a]	0.42	0.68	7.64	1.78	13.60
$Mo(CO)_3(AsPh_3)_2Cl_2$	19 [b]	1.06	0.33	0.62	2.50	1.55
$Mo(CO)_3(SbPh_3)_2Cl_2$	45 [b]	2.50	0.30	0.47	2.84	1.33
$Mo(CO)_3(PPh_3)_2Br_2$	1 [a]	0.003	0.35	1.03	2.67	2.75
$Mo(CO)_3(AsPh_3)_2Br_2$	7 [b]	0.38	0.26	0.50	3.00	1.50
$Mo(CO)_3(SbPh_3)_2Br_2$	33 [b]	1.83	0.27	0.46	3.04	1.40
$Mo(CO)_3(PPh_3)_2I_2$	13 [a]	0.04	0.42	1.19	2.49	2.96
$Mo(CO)_3(AsPh_3)_2I_2$	10 [b]	0.56	0.30	0.58	3.78	2.18
$Mo(CO)_3(SbPh_3)_2I_2$	17 [b]	0.94	0.26	0.72	6.18	4.45

Reaction time 0.67 h; [a] reaction time 100 h; [b] reaction time 6 h; yield (y) = 100% × {(mol of polymerised NBE) × (mol of NBE)$^{-1}$} [%]; average reaction rate (v_p) = (10^{-2} × yield) × (volume)$^{-1}$ × (reaction time)$^{-1}$ [mol dm^{-3} h^{-1}]; stereochemical parameters (σ_c, r_c, r_t, $r_c r_t$) were calculated as described in Ref. [10].

3. Results and discussion

The results of the ROMP experiments are summarized in Table 2.

All the complexes show some metathesis activity. Based on the similarity of the IR spectra, the structures of the initiators are closely related and differences in the catalytic properties may be attributed mainly to compositional variations.

The most remarkable observation is that within the relative small range of the composition studied the activity of the tungsten complexes is superior to their molybdenum analogs. The rate of the polymerization (V_p) varied between 7.8–32.9 $mol\,dm^{-3}\,h^{-1}$ in the case of the tungsten containing initiators with I/PPh_3 and $Br/AsPh_3$ ligand combinations representing the two extremes, respectively. The molybdenum complexes are about two orders of magnitude less active $(V_p = 0.003–2.50)$ having two extremes at Br/PPh_3 and $Cl/SbPh_3$ ligand combinations, respectively. The distribution of the cis and trans double bonds is blocky, $(r_c r_t > 1)$ for all catalysts, and $r_c r_t$ increases with cis content as previously found [12].

The molybdenum complexes with one exception (Cl/PPh_3), are more selective toward trans double formation $(\bar{\sigma}_c = 0.38)$, while the tungsten derivatives form the cis / trans isomers with nearly equal probability $(\bar{\sigma}_c = 0.52)$ allied with higher blockiness (Fig. 2). A change from trans to cis selectivity has also been noted when the Schrock initiator as precursor ligand $OC(CH_3)_3$ is changed to a harder analog, $OC(CF_3)_3$. The low c/t selectivity for the tungsten complexes is consisted with their much higher reactivity, indicating less discriminating propagating species.

Some trends may be recognized as a function of the ligands:

1. In the order of $L = PPh_3$, $AsPh_3$, $SbPh_3$ the reaction rate is increasing and the cis content of the polymers is decreasing in the case of the molybdenum initiators.

2. The cis selectivity and the catalytic activity of the tungsten complexes are highest for the $AsPh_3$ ligand.

3. The higher cis selectivity $(\sigma_c = 0.56–0.58)$ of the tungsten complexes provided by the I ligand is associated with significantly diminished activity. This is attributed to the relatively high bulkiness of the I ligand.

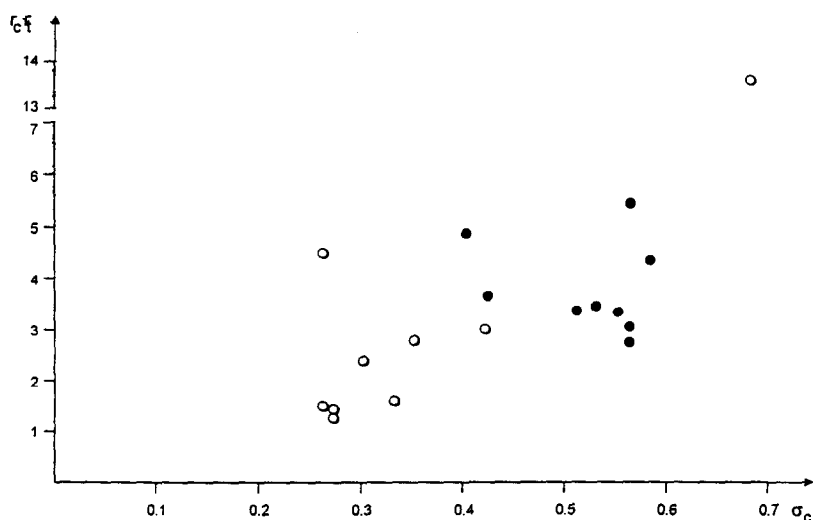Correlation between the $\bar{\nu}_{CO}$ of the precursors with catalytic characteristics (V_p, σ_c) were

Fig. 2. Plot of $r_c r_t$ against the fraction of double bonds having cis structure, σ_c. (●): W-, (○): Mo-based catalysts.

not found. Other electronic properties calculated by the Extended Hückel method [14] provided no grounds for rationalizing the results either.

The active species are as yet rather poorly characterized. However, some reliable experimental information shows that the catalytically active species contain at least one of each of the ligands (L and X) from the precursor.

Earlier studies revealed, that the precursor complexes are liable to loose a CO ligand when heated in solvent [15], but one or two CO ligands remain still in the coordination sphere of the transition metal as shown by the intramolecular carbene–CO coupling reactions [16]. The hydrocarbon part of the initiating carbene was identified as a 2-norbornylidene group [16,17]. Four kinds of ligand (L, X, $R^1R^2C=$ and CO), on the active center are identified by these direct and indirect experimental methods. It may now be deduced that the structure of the initiating carbene complexes is close to the one shown in Fig. 3 which is a 16 electron Schrock type carbene [18]. Isolation of the carbene complex is in progress.
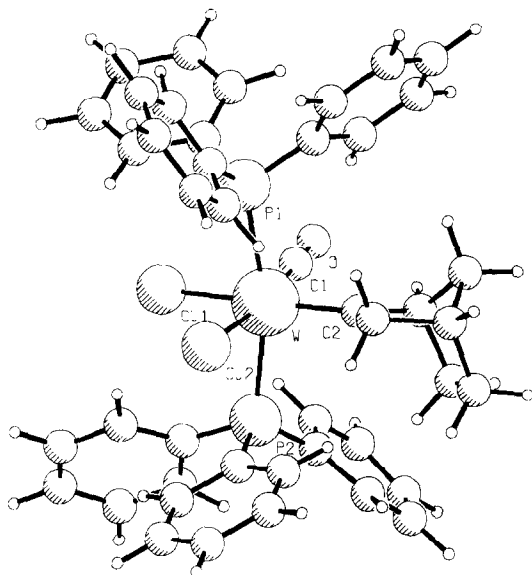

Fig. 3. Structure proposed for an initiating carbene (L = PPh$_3$, X = Cl).

4. Conclusion

A variety of $M(CO)_3X_2L_2$ (M = Mo or W; X = Cl, Br or I; L = PPh$_3$, AsPh$_3$ or SbPh$_3$) complexes may be activated thermally to initiate the metathesis polymerization of norbornene. At least one of each type of ligand of the precursor remains attached to the transition metal center of the active species.

Acknowledgements

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