polymers

MDPI

Metathesis Polymerization Reactions Induced by the Bimetallic Complex (Ph₄P)₂[W₂(μ-Br)₃Br₆]

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Abstract: The reactivity of the bimetallic complex (Ph₄P)₂[W₂(μ-Br)₃Br₆] ({W$^{\underline{2.5}}$W}$^{7+}$, a′²e³) towards ring opening metathesis polymerization (ROMP) of norbornene (NBE) and some of its derivatives, as well as the mechanistically related metathesis polymerization of phenylacetylene (PA), is presented. Our results show that addition of a silver salt (AgBF₄) is necessary for the activation of the ditungsten complex. Polymerization of PA proceeds smoothly in tetrahydrofuran (THF) producing polyphenylacetylene (PPA) in high yields. On the other hand, the ROMP of NBE and its derivatives is more efficient in CH₂Cl₂, providing high yields of polymers. ¹³C Cross Polarization Magic Angle Spinning (CPMAS) spectra of insoluble polynorbornadiene (PNBD) and polydicyclopentadiene (PDCPD) revealed the operation of two mechanisms (metathetic and radical) for cross-linking, with the metathesis pathway prevailing.

Keywords: metathesis; ROMP; metal-metal bonds; tungsten

1. Introduction

Metathesis reactions induce the mild cleavage/formation and redistribution of carbon-carbon double bonds and therefore allow for the synthesis of complex functional molecules in one-pot reactions. Among them, metathesis polymerization of alkynes [1–3] and ring opening metathesis polymerization (ROMP) of cycloolefins [4–6] yield unsaturated polymeric materials and are considered as two of the most important tools in polymer chemistry, leading to the synthesis of novel materials (Scheme 1). The properties of these polymers sensitively depend on their microstructure. This is, in effect, directly related to the stereoselectivity of the reaction, but tuning the conformation of polymers has been a long-standing problem [7,8]. Therefore, the choice of catalyst for each reaction is important, where high activity and selectivity need to be combined with functional group tolerance.

Scheme 1. Metathesis polymerization of alkynes (**left**) and Ring Opening Metathesis Polymerization (ROMP) of cycloolefins (**right**).

A wide range of catalytic systems have been explored, including uni-, bi-, and multicomponent ones, based mainly on mononuclear transition metal complexes along the periodic table (Ti, Nb, Ta, Cr, Mo, W, Re, Co, Ru, Os) [9,10]. In any case, the active catalytic species for metathesis polymerization reactions is a metallocarbene, which is either generated *in situ*, or has been previously synthesized and isolated, such as the well-defined Katz ([(OC)$_5$W = C(Ph)R]; R = OMe, Ph) [11,12], Schrock (Mo- and W-based) [13], and Grubbs (Ru-based) [14] alkylidenes and their numerous variations. Many of the catalytic systems in which metallocarbenes are formed *in situ* are ill-defined, because the exact nature of the active species remains unknown. Apart from homogeneous systems, immobilized (on polymeric or inorganic support) and recyclable catalysts have also been developed [15,16].

Bimetallic complexes with metal-metal bonds have been scarcely employed [17], although they provide more precise control over stereoselectivity, because both metal centers can be involved in the reaction. We have already reported that the ditungsten complex Na[W$_2$(μ-Cl)$_3$Cl$_4$(THF)$_2$]· (THF)$_3$ (**2**, {W$\underline{^3}$W}$^{6+}$, a$'^2$e$'^4$) is a highly efficient and stereoselective room temperature homogeneous and/or heterogeneous initiator for metathesis polymerization of alkynes [18] and ROMP of norbornene (NBE) and some of its derivatives [19]. That complex acts as a unicomponent initiator in most cases. Addition of small amounts of phenylacetylene (PA) generates a more reactive system, which is also more tolerant to coordinating side groups [20].

In view of exploring the potential catalytic reactivity of multiply-bonded transition metal complexes and establishing efficient, robust and stereoselective catalytic systems for metathesis polymerization reactions, we report a study of the reactivity of the perbromo-complex (Ph$_4$P)$_2$[W$_2$(μ-Br)$_3$Br$_6$] (**1**, {W$\underline{^{2.5}}$W}$^{7+}$, a$'^2$e$'^3$) towards the ROMP of NBE and some of its derivatives, as well as towards the mechanistically-related polymerization of PA. **1** is easily accessible, moderately air-stable, bears labile ligands and higher nuclear charge compared to **2**. Our results show that addition of a silver salt (AgBF$_4$) is required in order to activate the ditungsten complex. Comparison of the present catalytic system with that based on the structurally analogous **2** in terms of reactivity, as well as properties of the polymers formed, is also presented.

2. Materials and Methods

2.1. General

Starting materials were purchased from Sigma-Aldrich (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) and are of the highest available purities. (Ph$_4$P)[W(CO)$_5$Br] [21] and (Ph$_4$P)$_2$[W$_2$(μ-Br)$_3$Br$_6$] (**1**) [22] were prepared according to literature procedures. For the synthesis of both compounds, Ph$_4$PBr was used instead of ^{n}Pr$_4$NBr. PA was passed through an Al$_2$O$_3$ column and was distilled under vacuum. NBE was dissolved in the solvent used for the reaction, was dried by stirring with CaH$_2$ under argon, and it was distilled under vacuum prior to use. NBD, VNBE, and DCPD were dried by stirring with CaH$_2$ and they were distilled under vacuum. THF and Et$_2$O were distilled over Na/Ph$_2$CO, toluene, and hexane over Na, CH$_2$Cl$_2$ over CaH$_2$, and methanol over sodium methoxide. All solvents were distilled in an inert atmosphere, and were degassed by three freeze-pump-thaw cycles, with the exception of methanol, which was degassed by bubbling nitrogen or argon for 0.5 h. All operations were performed under a pure dinitrogen or argon atmosphere, using Schlenk techniques on an inert gas/vacuum manifold or in a drybox (O$_2$, H$_2$O <1 ppm).

UV-Vis spectra were recorded on Hitachi U-2000 (Hitachi High-Technologies Corporation, Tokyo, Japan) and Varian Cary 3E spectrophotometers (Varian Associates Inc, Mulgrave (Melbourne), Victoria, Australia). NMR spectra were recorded on a Varian Unity Plus 300 spectrometer (Varian Associates Inc., Palo Alto, CA, USA). In all cases, chemical shifts are reported in ppm relative to the deuterated solvent resonances. Size exclusion chromatography (SEC) experiments were carried out with a modular instrument consisting of a Waters model 600 pump, a Waters model U6K sample injector, a Waters model 410 differential refractometer and a set of 4 μ-Styragel columns with a continuous porosity range of 106–103 Å (Waters Corporation, Milford, MA, USA). The columns were housed in an oven thermostated at 40 °C. THF was the carrier solvent at a flow rate of 1 mL/min. The instrument was calibrated with PS standards covering the molecular weight range of 400–900,000. The thermal stability of the polymers was studied by thermogravimetric analysis (TGA) employing a Q50 TGA model from TA instruments (TA Instruments-Waters LLC, New castle, DE, USA). Samples were placed in platinum crucibles. An empty platinum crucible was used as a reference. Samples were heated from ambient temperatures to 600 °C in a 60 mL/min flow of N_2 at a heating rate of 10 °C/min.

Mass spectra were obtained on a Bruker UltrafleXtreme matrix assisted laser desorption ionization time-of-flight (MALDI-TOF) spectrometer (Bruker, Bremen, Germany) using *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. Spectra in the positive ion mode as well as in the negative ion mode were measured.

2.2. Catalytic Reactions

A typical procedure is described as follows. Monomer (e.g., PA; 653 μL, 608 mg, 6.0 mmol) was added to a solution of **1** (30.0 mg, 0.017 mmol) in a solvent (e.g., THF; 10.0 mL), followed by the silver salt ($AgBF_4$; 6.6 mg, 0.034 mmol) when employed. The mixture was allowed to react at room temperature for a given time, after which it was concentrated to half volume and treated with excess of methanol to have the polymeric products precipitated. The resulting solids were filtered and washed repeatedly with methanol. When it was possible, polymers were re-dissolved in THF and the above procedure was repeated at least three times. The products were dried *in vacuo*.

3. Results and Discussion

3.1. Catalyst Synthesis and Characterization

Compound **1** was synthesized from the reaction of $(Ph_4P)[W(CO)_5Br]$ and 1,2-dibromoethane in refluxing chlorobenzene, according to the literature procedure for the synthesis of the analogous $^nPr_4N^+$ salt [22], which features face-sharing bioctahedral (FSBO) geometry, with three terminal bromide ligands on each tungsten atom and three bridging ones (Scheme 2), and contains a metal-metal bond of order 2.5. Crystals of **1** suitable for X-ray analysis could not be obtained, but the complex was characterized by UV-Vis spectroscopy in CH_3CN (Figure S1) and MALDI-TOF mass spectrometry (Figure 1 and Figures S2–S6). UV-Vis spectra of both compounds (**1** and the $^nPr_4N^+$ salt) featured four peaks at the same wavelengths and with very similar molar absorption coefficients (Table S1). MALDI-TOF mass spectra in the positive ion region revealed fragments attributed to Ph_4P^+ and $[(Ph_4P)_3W_2Br_9]^+$, while in the negative ion region mononuclear and dinuclear fragments were observed (Table 1).
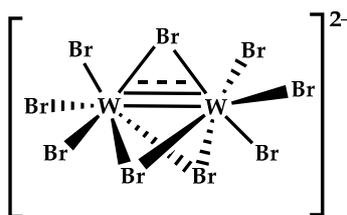
Scheme 2. Schematic representation of the dianion of complex **1**, $[W_2(\mu\text{-Br})_3Br_6]^{2-}$.
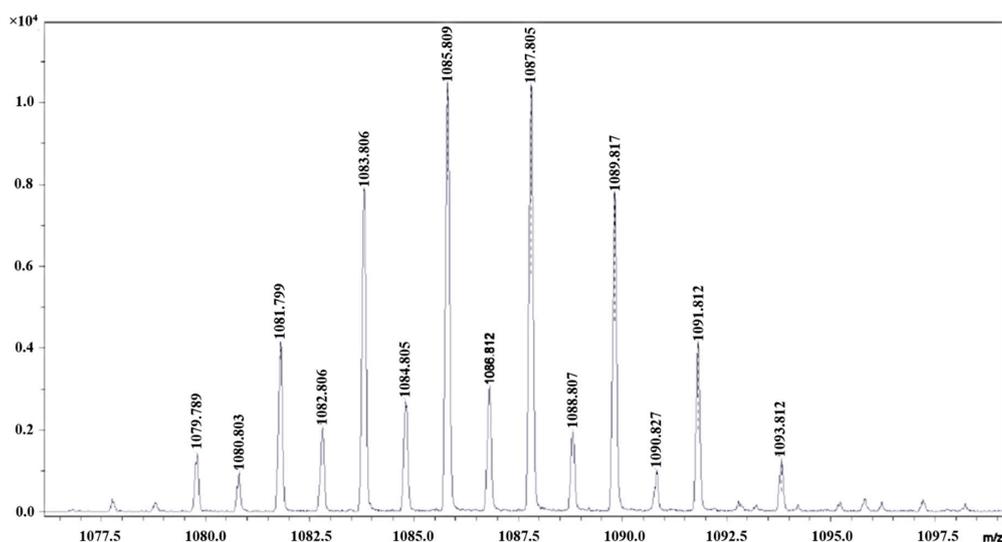
Figure 1. MALDI-TOF mass spectrum of **1** in *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (fragment $[W_2Br_9]^-$).

Table 1. Fragments (*m/z*) of **1**.

Fragment	*m/z* (Theoretical)	*m/z* (Experimental)
Ph_4P^+	339	339.213
$[(Ph_4P)_3W_2Br_9]^+$	2104	2106.932
$[W_2Br_9]^-$	1086	1085.809
$[Ph_4PW_2Br_9]^-$	1427	1427.563
$[WBr_5]^-$	583	582.207
$[W_2Br_7]^-$	926	925.977

1 is moderately air-sensitive (oxygen, moisture); in the solid state, it is stable in air at room temperature for a few hours. It is soluble in CH_2Cl_2 and CH_3CN, less soluble in tetrahydrofuran (THF) and $CHCl_3$, and insoluble in toluene and Et_2O. It was repeatedly recrystallized and checked carefully for purity (UV-Vis) before use.

3.2. Polymerization Reactions

Polymerization reactions were carried out at room temperature, for a given time, as shown in Tables 2–6. Monomers studied include phenylacetylene (PA), norbornene (NBE), 5-vinyl-2-norbornene (VNBE), norbornadiene (NBD) and dicyclopentadiene (DCPD). All possible products are shown in Scheme 3. Soluble polymers were characterized using ^{1}H NMR spectroscopy (Figures S7–S9) and insoluble polymers using ^{13}C Cross Polarization Magic Angle Spinning (CPMAS) spectroscopy. Addition of $AgBF_4$ was required, otherwise **1** was inactive towards polymerization reactions. The role of $AgBF_4$ was to remove one or more bromide ligands, thus generating vacant coordination sites at the bimetallic core, available for monomer coordination.

Table 2. Polymerization of phenylacetylene (PA) with the catalytic system **1**/AgBF$_4$.

Entry	Solvent	1/AgBF$_4$/PA Molar ratio	*t* (h)	Yield (%)	$M_n \times 10^{-3}$ [e]	M_w/M_n [e]	*cis* (%) [f]
1	CH$_2$Cl$_2$	1/2/350 [a]	24	9	5.2	1.45	0
2	CH$_2$Cl$_2$	1/3/350 [b]	24	12	4.6	1.37	0
3	CH$_2$Cl$_2$	1/4/350 [c]	24	20	2.8	1.89	0
4	THF	1/2/350 [a]	8	4	41.8	1.86	75
5	THF	1/2/350 [a]	16	88	67.8	1.60	77
6	THF	1/2/350 [a]	24	95	59.5	1.58	88
7	THF	1/3/350 [b]	2	13	70.5	1.72	85
8	THF	1/3/350 [b]	6	98	207	1.16	87
9	THF	1/3/350 [b]	8	79	54.2	1.61	85
10	THF	1/3/350 [b]	24	59	16.0	2.07	85
11	Toluene	1/3/350 [b]	24	_ [d]	_ [d]	_ [d]	_ [d]
12	CH$_3$CN	1/3/350 [b]	24	_ [d]	_ [d]	_ [d]	_ [d]

[a] Conditions: **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (6.6 mg, 0.034 mmol), PA (653 μL, 608 mg, 6.0 mmol), 10 mL solvent; [b] Conditions: **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (9.9 mg, 0.051 mmol), PA (653 μL, 608 mg, 6.0 mmol), 10 mL solvent; [c] Conditions: **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (13.2 mg, 0.068 mmol), PA (653 μL, 608 mg, 6.0 mmol), 10 mL solvent; [d] No polymer was isolated; [e] By SEC in THF at 40 °C *vs.* polystyrene standards; [f] As determined by ^{1}H NMR in CDCl$_3$.

Table 3. Polymerization of norbornene (NBE) with the catalytic system **1**/AgBF$_4$.

Entry	Solvent	1/AgBF$_4$/NBE Molar ratio	[NBE] (M)	*t* (h)	Yield (%)	$M_n \times 10^{-3}$ [g]	M_w/M_n [g]	*cis* (%) [h]
1	CH$_2$Cl$_2$	1/2/350 [a]	0.6	24	6	103.8	1.60	65
2	CH$_2$Cl$_2$	1/3/350 [b]	0.6	24	8	82.3	1.80	68
3	CH$_2$Cl$_2$	1/4/350 [c]	0.6	24	22	186.7	1.25	62
4	CH$_2$Cl$_2$	1/4/500 [d]	0.8	1	15	810.5	1.34	42
5	CH$_2$Cl$_2$	1/4/500 [d]	0.8	2	94	547.1	1.28	48
6	CH$_2$Cl$_2$	1/4/500 [e]	1.7	0.4	98	_ [i]	_ [i]	_ [i]
7	THF	1/4/500 [e]	1.7	24	_ [f]	_ [f]	_ [f]	_ [f]
8	CH$_3$CN	1/4/500 [e]	1.7	24	_ [f]	_ [f]	_ [f]	_ [f]

[a] Conditions: **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (6.6 mg, 0.034 mmol), NBE (565.0 mg, 6.0 mmol), 10 mL solvent; [b] Conditions: **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (9.9 mg, 0.051 mmol), NBE (565.0 mg, 6.0 mmol), 10 mL solvent; [c] Conditions: **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (13.2 mg, 0.068 mmol), NBE (565.0 mg, 6.0 mmol), 10 mL solvent; [d] Conditions: **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (13.2 mg, 0.068 mmol), NBE (800.0 mg, 8.5 mmol), 10 mL solvent; [e] Conditions: **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (13.2 mg, 0.068 mmol), NBE (800.0 mg, 8.5 mmol), 5 mL solvent; [f] No polymer was isolated; [g] By SEC in THF at 40 °C *vs.* polystyrene standards; [h] As determined by ^{1}H NMR spectra in CDCl$_3$; [i] Polymer insoluble in CHCl$_3$, CH$_2$Cl$_2$, THF.

Table 4. Polymerization of 5-vinyl-2-norbornene (VNBE) with the catalytic system **1**/AgBF$_4$.

Entry	Solvent	1/AgBF$_4$/VNBE Molar ratio	[VNBE] (M)	*t* (h)	Yield (%)	$M_n \times 10^{-3}$ [f]	M_w/M_n [f]
1	CH$_2$Cl$_2$	1/4/500 [a]	0.8	22	10	-	-
2	CH$_2$Cl$_2$	1/4/500 [b]	2.7	22	20	-	-
3	CH$_2$Cl$_2$	1/4/500 [c]	4.9	22	17	-	-
4	CH$_2$Cl$_2$	1/4/1000 [d]	2.3	26	Traces	-	-
5	CH$_2$Cl$_2$	1/4/2000 [e]	4.9	7	87	8.0	1.27
6	-	1/4/2000 [e]	-	23	39	16.7	1.16

[a] Conditions: **1** (30 mg, 0.017 mmol), AgBF$_4$: (13.2 mg, 0.068 mmol), VNBE (1.2 mL, 1.0 g, 8.5 mmol), 10 mL CH$_2$Cl$_2$; [b] Conditions: **1** (30 mg, 0.017 mmol), AgBF$_4$: (13.2 mg, 0.068 mmol), VNBE (1.2 mL, 1.0 g, 8.5 mmol), 2 mL CH$_2$Cl$_2$; [c] Conditions: **1** (30 mg, 0.017 mmol), AgBF$_4$: (13.2 mg, 0.068 mmol), VNBE (1.2 mL, 1.0 g, 8.5 mmol), 0.5 mL CH$_2$Cl$_2$; [d] Conditions: **1** (30 mg, 0.017 mmol), AgBF$_4$: (13.2 mg, 0.068 mmol), VNBE (2.4 mL, 2.0 g, 17 mmol), 2 mL CH$_2$Cl$_2$; [e] Conditions: **1** (30 mg, 0.017 mmol), AgBF$_4$: (13.2 mg, 0.068 mmol), VNBE (4.9 mL, 4.1 g, 34.0 mmol), 2 mL CH$_2$Cl$_2$ or bulk; [f] By SEC in THF at 40 °C *vs.* polystyrene standards.

Table 5. Polymerization of norbornadiene (NBD) with the catalytic system **1**/AgBF$_4$.

Entry	Solvent	1/AgBF$_4$/NBD Molar ratio	[NBD] (M)	*t* (h)	Yield (%)
1	CH$_2$Cl$_2$	1/2/500 [a]	1.7	0.75	72
2	CH$_2$Cl$_2$	1/4/500 [b]	1.7	1.5	92
3	CH$_2$Cl$_2$	1/4/500 [c]	3.4	21	98
4	CH$_2$Cl$_2$	1/8/500 [d]	1.7	4.5	95
5	THF	1/4/500 [b]	1.7	22	- [h]
6	THF	1/4/500 [c]	3.4	22	42
7	Toluene	1/4/500 [b]	1.7	23	traces
8	Toluene	1/4/1000 [e]	3.4	23	traces
9	Toluene	1/-/1000 [g]	3.4	4.5	80
10	Toluene	1/-/1000 [f]	3.4	4.5	traces
11	-	1/4/500 [b]	-	22	traces
12	-	1/4/1000 [e]	-	3	traces
13	-	1/-/1000 [g]	-	22	traces

[a] Conditions: **1** (30 mg, 0.017 mmol), AgBF$_4$ (6.7 mg, 0.035 mmol), NBD (0.8 mL, 725.0 mg, 8.5 mmol)/5 mL solvent; [b] Conditions: **1** (30 mg, 0.017 mmol), AgBF$_4$ (13.3 mg, 0.069 mmol), NBD (0.8 mL, 725.0 mg, 8.5 mmol), 5 mL solvent or bulk; [c] Conditions: **1** (30 mg, 0.017 mmol), AgBF$_4$ (13.3 mg, 0.069 mmol), NBD (0.8 mL, 725.0 mg, 8.5 mmol), 2.5 mL solvent; [d] Conditions: **1** (30 mg, 0.017 mmol), AgBF$_4$ (26.6 mg, 0.138 mmol), NBD (0.8 mL, 725.0 mg, 8.5 mmol), 5 mL solvent; [e] Conditions: **1** (30 mg, 0.017 mmol), AgBF$_4$ (13.3 mg, 0.069 mmol), NBD (1.6 mL, 1.4 g, 17 mmol), 2.5 mL solvent or bulk; [f] Conditions: **1** (30 mg, 0.017 mmol), NBD (1.6 mL, 1.4 g, 17 mmol), 2.5 mL solvent; [g] Conditions: **1** (30 mg, 0.017 mmol), NBD (1.6 mL, 1.4 g, 17 mmol), 2.5 mL solvent or bulk, reflux; [h] No polymer was isolated.

Table 6. Polymerization of dicyclopentadiene (DCPD) with the catalytic system **1**/AgBF$_4$.

Entry	Solvent	1/AgBF$_4$/DCPD Molar ratio	[DCPD] (M)	*t* (h)	Yield (%)
1	CH$_2$Cl$_2$	1/4/250 [a]	0.8	16	95
2	CH$_2$Cl$_2$	1/4/500 [b]	1.4	4	43
3	CH$_2$Cl$_2$	1/4/750 [c]	1.4	22	66
4	CH$_2$Cl$_2$	1/4/750 [d]	2.0	4	9
5	CH$_2$Cl$_2$	1/4/1000 [e]	2.6	22	15
6	Toluene	1/4/250 [a]	0.8	22	Traces
7	Toluene	1/4/500 [b]	1.4	22	53
8	Toluene	1/4/750 [d]	2.0	22	52
9	Toluene	1/4/1000 [e]	2.6	22	30
10	-	1/4/250 [a]	-	22	37
11	-	1/4/500 [b]	-	22	10
12	-	1/4/750 [d]	-	21	17
13	-	1/4/1000 [e]	-	21	47
14	Toluene	1/-/750 [f]	2.1	24	10
15	Toluene	1/-/1250 [f]	3.0	24	10

[a] Conditions: **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (13.2 mg, 0.068 mmol), DCPD (0.6 mL, 552.0 mg, 4.2 mmol)/5.0 mL solvent or bulk; [b] Conditions: **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (13.2 mg, 0.068 mmol), DCPD (1.2 mL, 1.1 g, 8.5 mmol)/5.0 mL solvent or bulk; [c] Conditions: **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (13.2 mg, 0.068 mmol), DCPD (1.8 mL, 1.7 g, 12.9 mmol)/7.4 mL CH$_2$Cl$_2$; [d] Conditions: **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (13.2 mg, 0.068 mmol), DCPD (1.8 mL, 1.7 g, 12.9 mmol)/5.0 mL solvent or bulk; [e] Conditions: **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (13.2 mg, 0.068 mmol), DCPD (2.4 mL, 2.2 g, 17.0 mmol)/5.0 mL solvent or bulk; [f] The reaction kept under reflux/Ar.
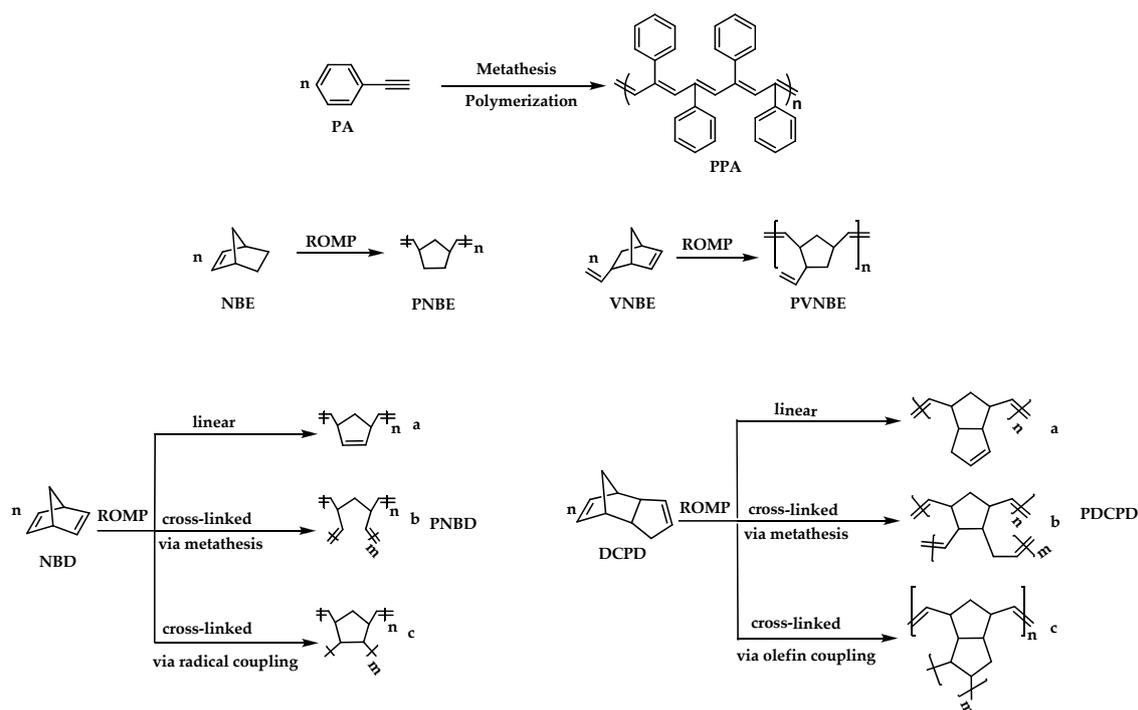
Scheme 3. Metathesis polymerization of PA and ROMP of NBE, VNBE, NBD and DCPD.

Polymerization of PA by **1**/AgBF$_4$ was studied in toluene, CH$_3$CN, CH$_2$Cl$_2$, and THF (Table 2). **1**/AgBF$_4$ was inactive in toluene and CH$_3$CN (entries 11 and 12). Toluene is a very poor solvent for both **1** and AgBF$_4$. CH$_3$CN is a strongly coordinating solvent and most likely prevented coordination of substrate to the bimetallic core. In CH$_2$Cl$_2$ (entries 1–3) similar results were obtained under all reaction conditions. The color of the reaction mixture gradually changed from green to the characteristic deep red color of polyphenylacetylene (PPA), but very low molecular weight polymers were isolated in low yields. Polymerization proceeded smoothly in THF when two equivalents of AgBF$_4$ were added, providing PPA in high yield after 24 h (entries 4–6). When the AgBF$_4$/**1** molar ratio was raised to 3/1, the polymerization proceeded faster and maximum yield was obtained after 6 h (entry 8). The molecular weight of PPA was higher than that of PPA obtained in CH$_2$Cl$_2$, whereas the molecular weight distribution was not much altered. At longer reaction times (entries 9 and 10), lower yields, lower molecular weights, and broader molecular weight distributions were observed. That could be attributed to depolymerization of PPA due to secondary metathesis and uncontrolled chain-transfer reactions, as was also observed with the catalytic system Na[W$_2$(μ-Cl)$_3$Cl$_4$(THF)$_2$]·(THF)$_3$ (**2**) [18]. Interestingly, the stereochemistry of polymers obtained changed from *all-trans* in CH$_2$Cl$_2$ to *high-cis* (77%–87%) in THF (Figure S7). Tuning the stereoselectivity of a catalytic system simply by changing the solvent is not frequently encountered. **2** exhibited similar behavior and provided mixtures of *cis* and *trans* PPA in CH$_2$Cl$_2$ and *high-cis* (90%) polymers in THF [18]. The molecular weights of PPA formed by both catalytic systems in THF were very similar, but the molecular weight distribution of PPA obtained in this this study was narrower. In CH$_2$Cl$_2$ the two catalytic systems differ significantly; as with **1**, reaction rate and molecular weights obtained were significantly lower.

ROMP of NBE was studied in CH$_3$CN, THF and CH$_2$Cl$_2$ (Table 3). The reaction did not proceed in THF and CH$_3$CN (entries 7 and 8). That could be attributed to: (a) the low solubility of **1**; and (b) the high coordinating ability of those solvents. In CH$_2$Cl$_2$ maximum yield was obtained for molar ratio **1**/AgBF$_4$/NBE equal to 1/4/500 (entries 5 and 6) with the reaction being faster at higher NBE concentrations (entry 6). The reaction was complete within minutes and provided polynorbornene

(PNBE) that was insoluble in common organic solvents, probably because of very high molecular weight. In more dilute solutions and with various AgBF$_4$/**1** molar ratios, polymerization was slower and yields were low to moderate (entries 1–4). The configuration of soluble polymers was determined by ^{1}H NMR spectroscopy (Figure S8) [19]. The fraction of *cis* double bonds (σ_c = 0.62) was estimated by integration of the signals at δ_H 2.79 (HC^{1,4} *cis*-PNBE) and 2.43 ppm (HC^{1,4} *trans*-PNBE). By comparison to **2** [19] or **2**/PA [20], the present catalytic system was less stereoselective, but provided quantitatively very high molecular weight polymers.

VNBE polymerization was studied only in CH$_2$Cl$_2$ (Table 4), because in that solvent the solubility of **1** was high and the polymerization of NBE was more efficient. The reaction rendered almost quantitative within a few hours (entry 5), when high molar ratio of VNBE/**1** and high [VNBE] were employed, but the molecular weight of poly(5-vinyl-2-norbornene) (PVNBE) obtained was low. At lower concentrations yields remained low, even after long reaction times (entries 1–4). In bulk, PVNBE with low molecular weight and very narrow molecular weight distribution was obtained in moderate yield (entry 6). The ^{1}H NMR spectrum of PVNBE (Figure S9) could not provide information about the configuration of the polymer, because signals of olefinic protons of the polymeric chain overlap with the vinylic ones, but indicated that the ring-strained C=C bond was cleaved, while the vinylic one was left intact and available for functionalization [23]. The same reactivity was observed with **2** [19] and **2**/PA [20] and is rather unusual. The pendant vinyl group is usually involved in metathesis reactions, leading to cross-linked products; therefore, that monomer is used for the synthesis of self-healing polymers [24]. Other than that, the reactivity of the catalytic systems was different, as very high (974,000) and high (97,000) molecular weight polymers were obtained with **2** and **2**/PA, respectively, although with much broader molecular weight distributions (2.6).

CH$_2$Cl$_2$ was found to be the optimum solvent for the ROMP of NBD (Table 5) as well. The reaction provided high yield of polynorbornadiene (PNBD) with molar ratio **1**/AgBF$_4$ equal to 1/2 (entry 1) and was quantitative, or almost quantitative, when molar ratios **1**/AgBF$_4$ equal to 1/4 or higher were employed (entries 2–4), but the rate was maximum when NBD concentration was equal to 1.7 M (entry 2), *i.e.*, under conditions identical to the polymerization of NBE. In THF, no reaction took place under the same conditions (entry 5), and when NBD concentration was higher (3.4 M), moderate yields were obtained (entry 6). In toluene, traces of polymer were obtained even after 23 h (entries 7 and 8). Interestingly, with **1**/NBD molar ratio equal to 1/1000, without adding AgBF$_4$, and under reflux, PNBD was obtained in high yield (80%; entry 9). Under similar conditions, but at room temperature, the reaction provided traces of PNBD (entry 10). Such reactivity resembles that of latent catalysts [25]. In bulk, traces of polymers were obtained in the presence or absence of AgBF$_4$, and even under reflux (entries 11–13). Molecular weights of polymers obtained could not be determined with size exclusion chromatography (SEC), because the polymers were insoluble. Differential thermogravimetry showed a bimodal decomposition peak at high temperatures (452 and 462 °C, respectively), indicating a high degree of crosslinking and a complex mechanism of thermal decomposition.

DCPD polymerization was studied in CH$_2$Cl$_2$, toluene, and in bulk (Table 6). Quantitative yield was obtained in CH$_2$Cl$_2$, with molar ratio **1**/DCPD equal to 1/250 (entry 1). When molar ratio and DCPD concentration were increased, yields were lowered (entries 2–5) and reaction times increased (entries 3 and 5). In toluene, after 22 h, yields were at best moderate. For molar ratios **1**/DCPD 1/500 and 1/750 (entries 7 and 8), polymer in almost 50% yield was obtained, while increasing or decreasing the ratio gave lower yields (entries 6 and 9). In contrast, polymers in 40%–50% yield were obtained in bulk, with ratios **1**/DCPD 1/250 and 1/1000 (entries 10 and 13). With molar ratios **1**/DCPD 1/500 and 1/750 the yields were much lower (entries 11 and 12). Two reactions in the absence of co-catalyst and with heating were made under conditions similar to those in the polymerization of NBD, but the yields were very low in both cases, despite the long reaction time (entries 14 and 15). Molecular weights of polydicyclopentadiene (PDCPD) obtained could not be determined with SEC, because polymers were insoluble. Differential thermogravimetry showed a bimodal decomposition

peak at high temperatures (462 and 470 °C respectively), indicating high degree of crosslinking and a complex mechanism of thermal decomposition, as in the case of PNBD polymers.

Regarding the ROMP of NBD, catalytic system **1**/AgBF$_4$ was almost equally reactive to **2**, which also provided quantitative yields within short reaction times [19,20]. In addition, it showed similar reactivity with **2**/PA towards the ROMP of DCPD [20], which seems to be the least reactive of the monomers studied, as long reaction times were required with either system.

Polymer characterization for insoluble polymers PNBD and PDCPD was done using ^{13}C CPMAS spectroscopy (Figures 2 and 3). Peaks at 133 (PNBD) and 129 (PDCPD) ppm are due to olefinic carbons, and peaks in the regions 30–53 (PNBD) and 26–60 ppm (PDCPD) are due to aliphatic carbons. Scheme 3 shows all possible products of NBD and PDCPD polymerization via ROMP. Polymers obtained may be linear or cross-linked. Cross-linked polymers are formed by reactions taking place on the double bond of the cyclopentene ring. Those can be either metathetic or olefin coupling reactions and have been well-studied for PDCPD [26]. The ratio of olefinic/aliphatic carbons depends on the mechanism of cross-linking and is equal to 4/3 (metathetic) and 2/5 (olefin coupling) for PNBD and 2/3 (metathetic) and 1/4 (olefin coupling) for PDCPD. Therefore, the olefin coupling contribution can be calculated by integration of the corresponding ^{13}C CPMAS peaks, and by using the following equations for PNBD (Equation (1)) and PDCPD (Equation (2)) [27]. In those equations C$_{olefinic}$ refers to carbons of double bonds, C$_{aliphatic}$ to carbons of single bonds, and *x* is the fraction of polymer double bonds that participate in cross-linking via olefin coupling. Integration of the PNBD spectrum provided a ratio of 1/0.93 and integration of the PDCPD spectrum provided a ratio of 1/1.81. By replacing the experimental values in Equations (1) and (2); *x* = 0.19 for PNBD and *x* = 0.22 for PDCPD, *i.e.*, 19% of NBD and 22% of DCPD double bonds participated in crosslinking via olefin coupling.

$$(4 - 2x)/(3 + 2x) = [\text{C}_{olefinic}/\text{C}_{aliphatic}]_{experimental} \tag{1}$$

$$(2 - x)/(3 + x) = [\text{C}_{olefinic}/\text{C}_{aliphatic}]_{experimental} \tag{2}$$
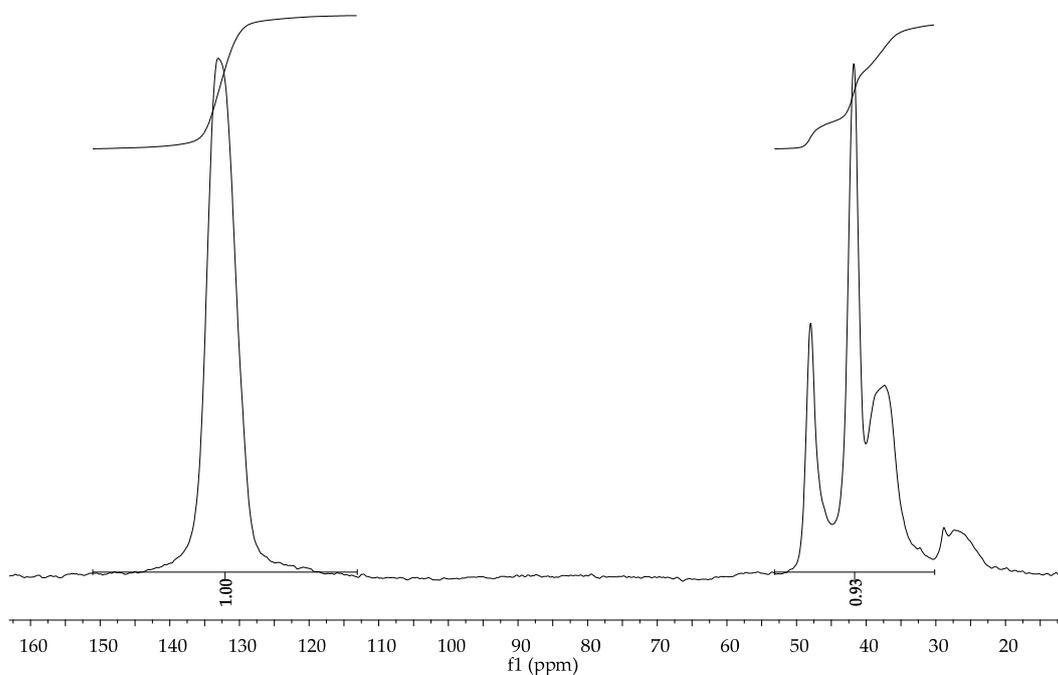
Figure 2. ^{13}C Cross Polarization Magic Angle Spinning (CPMAS) spectrum of PNBD obtained from the reaction of **1**/AgBF$_4$/NBD (Table 5, entry 4) in CH$_2$Cl$_2$.
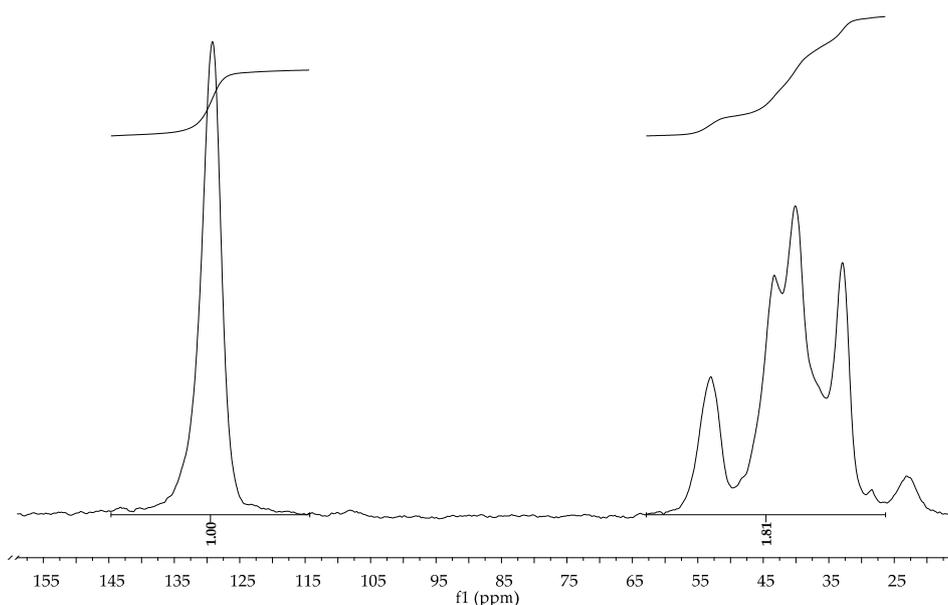
Figure 3. ^{13}C CPMAS spectra of PDCPD obtained from the reaction of **1**/AgBF$_4$/DCPD (Table 6, entry 1) in CH$_2$Cl$_2$.

3.3. Kinetic Studies

The progress of reaction of each monomer, with the exception of NBE polymerization, which was very rapid, was monitored by measuring the polymerization yield gravimetrically, and the molecular characteristics of the polymers formed (number average molecular weight and molecular weight distribution) by SEC analysis. Results for PA polymerization in THF using a molar ratio **1**/AgBF$_4$/PA equal to 1/3/350 are displayed in Table S2 and Figure 4. It is obvious that the yield increased more or less linearly with time up to quantitative conversion in 6 h. In the same time the molecular weight increased to high values, whereas the molecular weight distribution diminished rapidly. Longer polymerization times, up to 24 h, lead to scission of the produced polymeric chains and therefore to lower yields of polymerization along with lower molecular weights and broader distributions. This behavior is similar to that observed during the polymerization of PA with the triply bonded complex **2** in THF solutions [18]. In the present study, the maximum yield and molecular weight were observed in ~6 h of polymerization, whereas in the previous study in ~2 h. Therefore, **1** polymerized PA with a lower rate, but the reaction was more controlled, leading to products of higher molecular weight and considerably smaller molecular weight distributions.
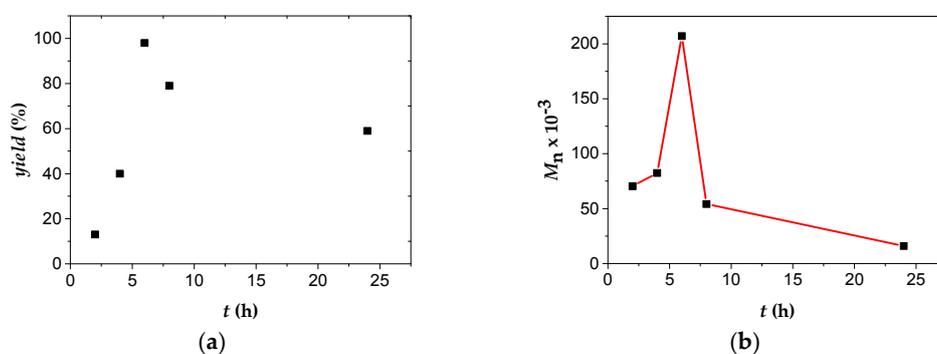
Figure 4. Polymerization of PA (653 μL, 608 mg, 6.0 mmol) with **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (9.9 mg, 0.051 mmol) and 10 mL THF (25 °C); (**a**) % yield *vs.* time plot of PPA; (**b**) $M_n \times 10^{-3}$ *vs.* time plot.

Variation of polymerization yield with time for NBD is given in Figure 5, whereas data are displayed in Table S3. Apparently, the system was characterized by an induction period, which was equal to a few minutes. This period was devoted to the complexation of the monomer to the catalyst and the initiation step of the polymerization process. After this period, the yield increased linearly with time. Nearly quantitative yields were obtained after 90 min of reaction. This result indicates that both the polymerization reaction through the opening of the first double bond and the cross-linking reaction occuring at the second double bond proceeded smoothly with time and simultaneously in the same manner leading to a controlled synthesis of cross-linked PNBD.
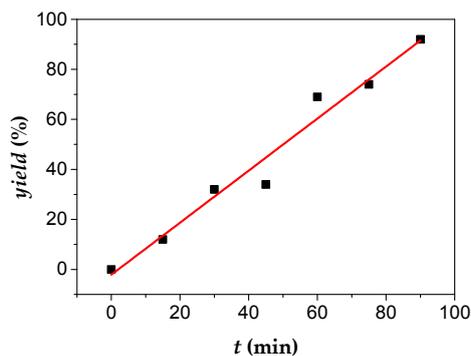
Figure 5. Polymerization of NBD (0.8 mL, 725.0 mg, 8.5 mmol) with **1** (30 mg, 0.017 mmol), AgBF$_4$ (13.3 mg, 0.069 mmol) and 5 mL CH$_2$Cl$_2$ (25 °C); % yield *vs.* time plot of PNBD.

The kinetics of polymerization of VNBE was studied in CH$_2$Cl$_2$ solutions, as shown in Table S4 and Figure 6. As in the case of NBD polymerization, an induction period was also observed for VNBE polymerization, indicating that the same mechanism took place in both cases. Compared to NBD, the initiation, as well as the propagation reaction, proceeded in a slower manner, probably due to the increased steric hindrance of VNBE. However, the yield scaled linearly with time indicating that the polymerization reaction proceeded in a well-controlled way.
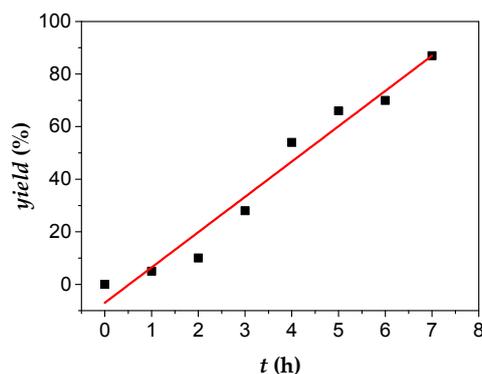
Figure 6. Polymerization of VNBE (4.9 mL, 4.1 g, 34.0 mmol) with **1** (30 mg, 0.017 mmol), AgBF$_4$ (13.2 mg, 0.068 mmol) and 2 mL CH$_2$Cl$_2$; % yield *vs.* time plot of PVNBE.

The initiation reaction for DCPD was very fast, since the plot of yield *vs.* time passed through the origin, as shown in Figure 7 and Table S5. The polymerization rate was initially very fast without the presence of an appreciable induction period. However, upon progressing time, the rate of polymerization was substantially lowered. Compared to other monomers examined in this work, DCPD was the less reactive, probably due to the increased steric hindrance of this monomer. Retardation of the polymerization may be attributed to the increased time needed for the activation of the second double bond of the monomer leading to cross-linked products.
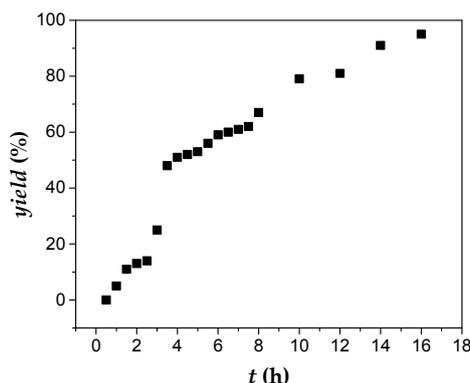
Figure 7. Polymerization of DCPD (0.6 mL, 552.0 mg, 4.2 mmol) with **1** (30.0 mg, 0.017 mmol), AgBF$_4$ (13.2 mg, 0.068 mmol) and 5.0 mL CH$_2$Cl$_2$; % yield *vs.* time plot of PDCPD.

4. Conclusions

The ditungsten complex (Ph$_4$P)$_2$[W$_2$(μ-Br)$_3$Br$_6$] (**1**) was successfully employed for the metathesis polymerization of phenylacetylene (PA) and the ROMP of norbornene (NBE) and some of its derivatives. Addition of AgBF$_4$ as a co-catalyst was necessary for the activation of **1** via abstraction of bromide ligands. PA polymerization proceeded smoothly in a mildly coordinating solvent like THF (but not in MeCN, which is a stronger donor) quantitatively producing PPA with high molecular weight and very narrow molecular weight distribution (1.16). The polymeric products obtained featured high *cis* content (>80%). On the contrary, in CH$_2$Cl$_2$, oligomers were formed, most likely due to PPA depolymerization, a trend that was previously observed for Na[W$_2$(μ-Cl)$_3$Cl$_4$(THF)$_2$]·(THF)$_3$ (**2**) [18].

NBE is significantly less reactive than PA, and as a result, ROMP of NBE did not take place in THF. In the latter case, a non-coordinating solvent, *i.e.*, CH$_2$Cl$_2$, was used, and PNBE and derivatives were formed in high yields, when the stoichiometric ratio was properly adjusted in order to avoid gelation of reaction mixtures. In comparison to **2**, which is an efficient and stereoselective catalyst (formation of polymers with high *cis* content was favored) for ROMP [19], **1**/AgBF$_4$ was equally effective with respect to yields, but exhibited lower selectivity. However, **1** is less sensitive to moisture and oxygen and it can be prepared more easily.

Other notable features of **1**/AgBF$_4$ reactivity are:

(a) Short reaction times (15 min–3 h), of all monomers except for VNBE (23 h).

(b) PVNBE contained all pendant vinyl bonds intact, had low molecular weight (M_w = 8000), but also narrow molecular weight distribution (M_w/M_n = 1.27), the lowest reported so far.

(c) Polymerization of NBD could proceed in toluene without addition of co-catalyst (reflux, less than 5 h and 80% yield). That result was important and will be further investigated, because catalytic systems in which components may coexist, but they do not react unless the system is heated, are of particular industrial interest.

(d) PNBD and PDCPD were insoluble and highly cross-linked, as evidenced by thermogravimetric analysis. ^{13}C CPMAS spectra revealed the operation of two mechanisms (metathetic and radical) for cross-linking, with metathesis being the major pathway (~80%). A full mechanistic study is underway.

from the reaction of **1**/AgBF$_4$/PA (Table 1, entry 6) in THF; Figure S8. ^{1}H NMR spectrum (CDCl$_3$) of PNBE obtained from the reaction of **1**/AgBF$_4$/NBE (Table 2, entry 3) in CH$_2$Cl$_2$; Figure S9. ^{1}H NMR spectrum (CDCl$_3$) of PVNBE obtained from the reaction of **1**/AgBF$_4$/VNBE (Table 3, entry 5) in CH$_2$Cl$_2$; Table S1: UV-Vis spectroscopic data of **1** (C = 2.09 × 10^{-4} M). In brackets the values from the literature of the analogous compound (^{n}Pr$_4$N)$_2$[W$_2$(μ-Br)$_3$Br$_6$]; Table S2. Polymerization of PA with the catalytic system **1**/AgBF$_4$; Table S3. Polymerization of NBD with the catalytic system **1**/AgBF$_4$; Table S4. Polymerization of VNBE with the catalytic system **1**/AgBF$_4$; Table S5. Polymerization of DCPD with the catalytic system **1**/AgBF$_4$.

Author Contributions: Patrina Paraskevopoulou and Konstantinos Mertis were responsible for this study and participated in its design. Despoina Christi, Alexios Grigoropoulos, and Grigorios Raptopoulos synthesized and characterized compound **1** and the polymers. Marinos Pitsikalis characterized the polymers and analyzed the kinetic data. Georgios Charalambidis, Vasilis Nikolaou and Athanassios G. Coutsolelos performed the MALDI-TOF experiments and analyzed the data. All authors were involved in reading and approving the final manuscript.

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