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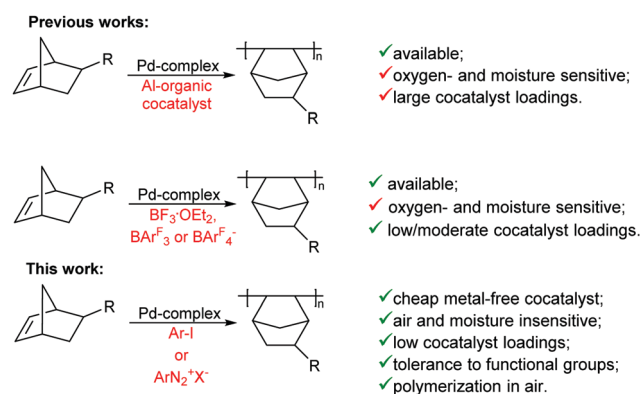## Activation of Pd-precatalysts by organic compounds for vinyl-addition polymerization of a norbornene derivative†

Gleb O. Karpov,[a] Xiang-Kui Ren, [b] Elizaveta K. Melnikova[cd] and Maxim V. Bermeshev [*a]

An approach to activating Pd-complexes without using additives such as Lewis acids has been developed for addition polymerization of norbornenes. Aryl iodides and aryl diazonium salts were efficiently applied as cocatalysts to Pd(0)- and Pd(2+)-complexes. The developed systems catalyzed polymerization of norbornenes containing bulky and polar functional groups both in an inert atmosphere and air resulting in soluble and high-molecular-weight saturated polymers.

Vinyl-addition polymerization of cycloolefins (cyclopropenes,[1] cyclobutenes,[2] cyclopentene,[3] norbornene and its derivatives,[4–6] cycloallenes,[7] etc.[8]) is a powerful tool for the design of polymers with saturated and rigid main chains. These polymers possess high thermal and chemical stability, high T_g, good transparency and low water uptake. The rigid nature of these polymers' backbones facilitates the formation of porosity and large free volume. The properties of such kinds of polymers can be finely tuned by introducing appropriate functional groups to side-chains. Among cycloolefins, norbornene derivatives are distinguished by the desirable combination of high polymerization reactivity, preparative availability of monomers and versatile chemistry of their synthesis. These cycloolefins are polymerized according to ROMP and vinyl-addition schemes of polymerization. In sharp contrast to ROMP polymerization of norbornenes,[9,10] the development of simple, stable and efficient catalytic systems remains a key issue in the synthesis of vinyl-addition polynorbornenes. Now, catalysts used in vinyl-addition polymerization of norbornenes can be divided into two groups (Scheme 1). The first one is single component catalysts not demanding addition of a cocatalyst.[11–13] These catalysts (*e.g.* (η^6-toluene)Ni(C$_6$F$_5$)$_2$,[11,14] (Ph$_3$Sb)$_2$Ni(C$_6$F$_5$)$_2$,[15] *etc.*) exhibit moderate catalytic activity and are easy to use, but they are sensitive to oxygen/water and not readily available. The second group of catalysts is early and late transition metal complexes/salts (precatalysts) activated by a Lewis acid (perfluorinated boranes, alumino-organic compounds or their combination),[11,16] a borate (Li$^+$[B(C$_6$F$_5$)$_4$]$^-$, Na$^+$[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$, *etc.*)[12,17–19] or another inorganic salt containing a large weakly coordinating anion (*e.g.*, AgSbF$_6$).[11,12,20–22] Such cocatalysts are necessary for halogen/ligand abstraction from a metal complex, charge compensation, the formation of an easily accessible coordination site and subsequent generation of truly active catalytic species containing metal–carbon or metal–H bonds. These systems usually polymerize norbornenes with good or high catalytic activity. However, cocatalysts applied to activate metal complexes are often water and oxygen sensitive, complicating polymerization and imposing some restrictions on their usage.

The application of organometallic cocatalysts also increases the content of catalyst residues in the resulting polymer. This

[a] *A. V. Topchiev Institute of Petrochemical Synthesis RAS, 29, Leninskii Prospect, Moscow, 119991, Russia. E-mail: bmv@ips.ac.ru*

[b] *School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300350, P. R. China*

[c] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov Street 28, Moscow, 119991, Russia*

[d] *M. V. Lomonosov Moscow State University, Department of Chemistry, Leninskie Gory 1, Russia*

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Scheme 1 The main approaches to activation of Pd-complexes for vinyl-addition polymerization of norbornenes.

leads to deterioration of some operational properties and limits the scope of the synthesized polymers. In this work, we describe the first examples of the activation of metal complexes for vinyl addition polymerization by readily available and simple organic compounds. The suggested approach is based on using organic Ar–X compounds (X–halogen, OTf, $N_2^+OTf^-$ or $N_2^+BF_4^-$) containing reactive C–X bonds as cocatalysts for vinyl addition polymerization instead of the above-mentioned organometallic or organoelement cocatalysts.

We started the investigations with polymerization of unsubstituted norbornene (NB) over the Pd(dba)$_2$ complex as a precatalyst activated by various ArX and AlkX compounds (Table S1, ESI†).[23] Although it is well known that various ArX and AlkX derivatives are capable of undergoing efficient oxidative addition to Pd(0)-complexes,[24–26] the realization of this step turned out to be insufficient for polymerization of NB. Further initiation of polymer chain growth by the activated Pd-species is required. As a result, the efficiency of activation of the Pd(0)-complex for polymerization of NB dramatically depended on the nature of the organic compound. The polymer was obtained over Pd(dba)$_2$ in the presence of only phenyl iodide as a cocatalyst with a reasonable yield (Table S1 and Fig. S1, ESI†). In the meantime, other cocatalysts tested (ArX or AlkX) did not show significant efficiency of activation. Utilizing most of the catalytic system based on chlorides and bromides barely resulted in polymer formation (Table S1, ESI†).

A disubstituted benzene derivative containing both a halogen and an electron-withdrawing group as substituents turned out to be a noticeably more efficient cocatalyst. The incorporation of an electron-withdrawing group, for example, –NO$_2$ or –CF$_3$, into phenyl iodide resulted in an essential increase in the efficiency of the cocatalyst (Table 1). The system Pd(dba)$_2$/p-NO$_2$C$_6$H$_4$I was found to be effective for polymerization of NB at high monomer/Pd molar ratios. At the same time, the activation of Pd(dba)$_2$ by aryl halides with electron-donating

substituents unexpectedly gave only traces of polynorbornene (Table S1, ESI†).

Adjustment of the catalyst system activity could be achieved by varying the molar ratio of Pd(dba)$_2$ and p-NO$_2$C$_6$H$_4$I (Table 1). Interestingly the monomer concentration had a strong influence on the rate of polymerization (Table 1 and Fig. 1), while the molecular weights of the resulting polymers only slightly changed.

A further improvement in catalytic activity was achieved by using aryl diazonium salts as cocatalysts (Table 2). As in the case of aryl halides, the activity of the Pd(dba)$_2$/aryl diazonium salt system strongly depended on the nature of the aryl diazonium salt and monomer concentration (Fig. S2, ESI†). Aryl diazonium tetrafluoroborates with an electron-withdrawing substituent in the aryl ring were found to be significantly more efficient cocatalysts probably due to their higher reactivity and less stability. Interestingly, the BF$_4^-$ anion could not activate Pd-complexes in addition polymerization in contrast to previously used organoboranes and organoborates with (per)fluorinated aryl substituents connected to the boron atom. The application of NaBF$_4$ as a cocatalyst led only to traces of the polymer under the same reaction conditions. Moreover, no synergetic effect was observed when simultaneously NaBF$_4$ and p-NO$_2$C$_6$H$_4$I were used as a combined cocatalyst for the activation of Pd(dba)$_2$. The molar ratio of the aryl diazonium salt/Pd(dba)$_2$ system exerted less effect on the catalytic activity (Table S2, ESI†) than was observed in the case of aryl halides as cocatalysts. This may indicate a more productive activation of a Pd-complex by aryl diazonium salts in comparison to aryl halides. Aryl diazonium salt/Pd(dba)$_2$ systems efficiently catalyzed polymerization of NB at much higher monomer/Pd molar ratios than aryl halide/Pd(dba)$_2$ systems did. Besides noticeably higher catalytic activity, these cocatalysts provided both high yields and high molecular weights of the resulting polymers. The polymer yields slightly increased with increasing monomer concentration in the range of 2–3 M and it sharply decreased with monomer concentration in the range of monomer concentration below 2–3 M (Fig. S2, ESI†). Usually, high molecular weight addition polynorbornene is poorly soluble in common organic solvents or

Table 1 Addition polymerization of NB using a Pd(dba)$_2$/p-NO$_2$C$_6$H$_4$I catalytic system[a]

NB/Pd molar ratio	Pd(dba)$_2$/p-NO$_2$C$_6$H$_4$I molar ratio	[NB], M	Yield, %	M_w ($\times 10^{-3}$)	M_w/M_n[b]
100	1/1	3.6	29	—	—
	1/3	3.6	68	5.7	1.7
	1/5	3.6	75	5.7	1.7
	1/10	3.6	85	6.1	1.7
	1/20	3.6	83	—	—
300	1/3	6.2	43	11.7	1.8
	1/3	3.9	32	9.6	1.8
500	1/3	6.2	36	11.3	1.7
	1/3	3.9	21	8.3	1.9
	1/3		93[c]	—	—
1000	1/3	6.2	Traces	—	—
	1/3	3.9	Traces	—	—
	1/3		84[c]	5.3	1.9

[a] The polymerization conditions: 25 °C, 2 h, monomer/Pd molar ratio = 100/1, [NB] = 3.6 M; the solvent – toluene; in argon. [b] Molecular weights and PDI were determined by GPC according to polystyrene standards. [c] The reaction time was 24 h.
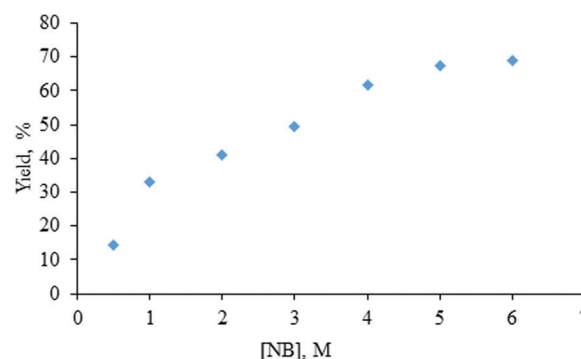

Fig. 1 The influence of NB concentration on the polynorbornene yield (catalyst – Pd(dba)$_2$/p-NO$_2$C$_6$H$_4$I; monomer/Pd molar ratio = 100/1; molar ratio of Pd(dba)$_2$/p-NO$_2$C$_6$H$_4$I = 1/3; the solvent – toluene; the reaction time – 2 h; in argon).

Table 2 The influence of aryl diazonium salt structure on the activity of a Pd(dba)$_2$-based catalytic system[a]

Cocatalyst	NB/Pd molar ratio	Time, h	Yield, %	M_w ($\times 10^{-3}$)	M_w/M_n
PhN$_2$$^+OTf^-$	250/1	24	20	—	—
PhN$_2$$^+BF_4$$^-$	1000/1	0.25	8	16	1.3
	2000/1	0.75	10	23	1.4
	3000/1	2	Traces	—	—
p-CF$_3$-C$_6$H$_4$N$_2$$^+BF_4$$^-$	1000/1	0.25	76	59	1.6
	2000/1	0.75	30	51	1.5
	3000/1	2	18	50	1.7
p-NC-C$_6$H$_4$N$_2$$^+BF_4$$^-$	1000/1	0.25	26	28	1.3
	2000/1	0.75	58	73	1.4
	3000/1	2	50	69	1.4
p-NO$_2$-C$_6$H$_4$N$_2$$^+BF_4$$^-$	1000/1	0.25	72	55	1.3
	2000/1	0.75	84	71	1.4
	3000/1	2	44	62	1.3

[a] [NB] = 2 M; molar ratio of Pd(dba)$_2$/p-XC$_6$H$_4$N$_2$$^+A^-$ (A$^-$ = BF$_4$$^-$ or OTf$^-$) = 1/3; the solvent – CHCl$_3$, the reaction temperature – 25 °C; in air.

Table 3 Polymerization of NB using different Pd-precatalysts activated by organic compounds[a]

Precatalyst	Cocatalyst	Yield, %	M_w ($\times 10^{-3}$)	M_w/M_n
Pd(dba)$_2$	p-NO$_2$C$_6$H$_4$I	96	5.7	1.7
	p-NO$_2$C$_6$H$_4$N$_2$$^+BF_4$$^-$	99	83	1.6
Pd$_2$(dba)$_3$	p-NO$_2$C$_6$H$_4$I	96	5.9	1.7
	p-NO$_2$C$_6$H$_4$N$_2$$^+BF_4$$^-$	99	109	1.8
SIPrPdPCy$_3$	p-NO$_2$C$_6$H$_4$N$_2$$^+BF_4$$^-$	Traces	—	—
Pd(PPh$_3$)$_4$	p-NO$_2$C$_6$H$_4$I	7	0.6	1.1
	p-NO$_2$C$_6$H$_4$N$_2$$^+BF_4$$^-$	90	90	1.9
Pd(OAc)$_2$	p-NO$_2$C$_6$H$_4$I	97	4.8	1.9
	p-NO$_2$C$_6$H$_4$N$_2$$^+BF_4$$^-$	79	—	—
Pd(acac)$_2$	p-NO$_2$C$_6$H$_4$I	Traces	—	—
	p-NO$_2$C$_6$H$_4$N$_2$$^+BF_4$$^-$	Traces	—	—
PdCl$_2$	p-NO$_2$C$_6$H$_4$I	20	1.1	1.3
	p-NO$_2$C$_6$H$_4$N$_2$$^+BF_4$$^-$	Traces	—	—

[a] For p-NO$_2$C$_6$H$_4$I as a cocatalyst, the conditions of polymerization were: [NB] = 3.2 M; NB/Pd molar ratio = 100/1; molar ratio of a Pd/cocatalyst = 1/3; the solvent – toluene, reaction time – 16 h, 25 °C, in argon. For p-NO$_2$C$_6$H$_4$N$_2$$^+BF_4$$^-$ as a cocatalyst, the conditions of polymerization were: p-NO$_2$C$_6$H$_4$N$_2$$^+BF_4$$^-$ [NB] = 1 M; NB/Pd molar ratio = 1000/1; molar ratio of Pd/cocatalyst = 1/3; the solvent – chloroform, reaction time – 16 h, 25 °C, in air.
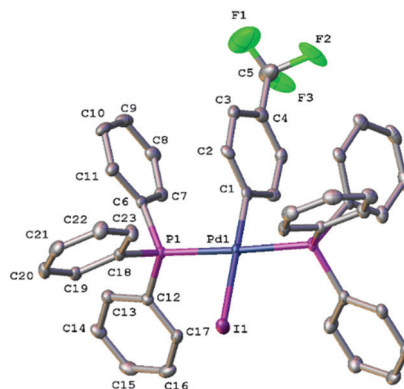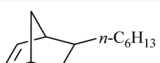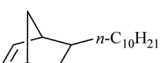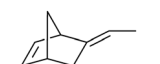

Fig. 2 General view of (p-CF$_3$C$_6$H$_4$)Pd(PPh$_3$)$_2$I in the representation of non-hydrogen atoms as thermal ellipsoids at a 50% probability level according to X-ray analysis.

even insoluble at all.[11,16] Herein, the polynorbornene, prepared with using the Pd-system activated by an organic compound, is well soluble in chloroform producing thin, robust freestanding films *via* a solution casting method.

The polymerization temperature and the nature of the solvent also exerted a strong influence on the catalytic activity (Table 2 and Tables S3, S4, ESI†). The polymerization in non-polar toluene proceeded very slowly, while in 1,2-dichloroethane the resulting polymer was insoluble and precipitated during the polymerization, which reduced the catalytic activity. The increase in polymerization temperature led to lower yields, possibly due to catalyst decomposition.

The next challenging issue was to evaluate the scope of the developed approach for vinyl-addition polymerization. To extend the approach under study, we tested out activation of different Pd(0)- and Pd(2+)-complexes with Ar–X compounds that were found to generate active species in the presence of Pd(dba)$_2$.

The studied organic cocatalysts activated Pd(0)-complexes and even some Pd(2+)-complexes (Table 3). In the case of Pd(2+)-complexes, it is likely that activation proceeded through a transformation of a Pd(2+)-complex into a Pd(0)-complex followed by the oxidative addition of a cocatalyst. The reduction of a Pd(2+) to a Pd(0)-complex by aryl halides has been earlier studied.[27]

Interestingly, a Pd-complex ((p-CF$_3$C$_6$H$_4$)Pd(PPh$_3$)$_2$I, Fig. 2) formed upon the addition of the first molecule of p-CF$_3$C$_6$H$_4$I to Pd(PPh$_3$)$_4$ did not catalyze polymerization of norbornene. Therefore, an excess of cocatalyst is required to form truly active Pd-species.

Another task was to extend the range of the norbornene-type monomers able to be involved in polymerization in the presence of the studied catalytic systems. Systems based on a Pd-complex activated by an aryl halide or aryl diazonium salt were able to catalyze vinyl-addition polymerization of substituted norbornenes containing both bulky hydrocarbonic-groups and polar reactive groups such as a carboxy group (Table 4). The corresponding polymers were successfully isolated with moderate or good yields and exhibited rather narrow molecular-weight distributions. Furthermore, polymerization of NB and its derivatives was readily conducted in both air and an inert atmosphere (argon), which makes the developed systems easy to handle and promising for the following studies.

The proposed mechanism of addition polymerization is shown in Scheme 2. The reaction is initiated by oxidative addition of an Ar–X compound to a Pd(0)-complex, generating Ar–Pd(2+)–X species. These species undergo carbopalladation with the first molecule of NB. These stages are common for Cattelani reaction and for vinyl-addition polymerization. In the next steps, the abundance of NB makes sequential insertion of many norbornene molecules into a Pd–C-bond likely to occur, which, in turn, leads to the formation of addition polynorbornene. Meanwhile the lack of NB together with the presence of a base, electrophilic and terminating reagents, directs the process into a Catelanni reaction with formation of a C–H functionalized arene.
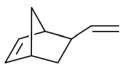
Table 4 Addition polymerization of substituted norbornenes in the presence of the Pd(dba)$_2$/p-NO$_2$C$_6$H$_4$N$_2$$^+BF_4$$^-$ system[a]

Monomer	Media	Yield, %	$M_w \times 10^{-3}$	M_w/M_n
n-C$_6$H$_13$	Ar	96	47	2.0
	Air	95	42	2.1
n-C$_{10}$H$_{21}$	Ar	80	44	2.2
	Air	95	—	—
	Air	18	—	—
—COOH	Ar[c]	55	—	—
	Air[b]	53	—	—

[a] The conditions of polymerization were: [monomer] = 3.0 M; monomer/Pd molar ratio = 250/1; molar ratio of p-NO$_2$C$_6$H$_4$N$_2$$^+BF_4$$^-$/Pd(dba)$_2$ = 3/1; the solvent – chloroform; reaction time – 30 min; 25 °C. [b] The reaction time – 4 h, 45 °C.
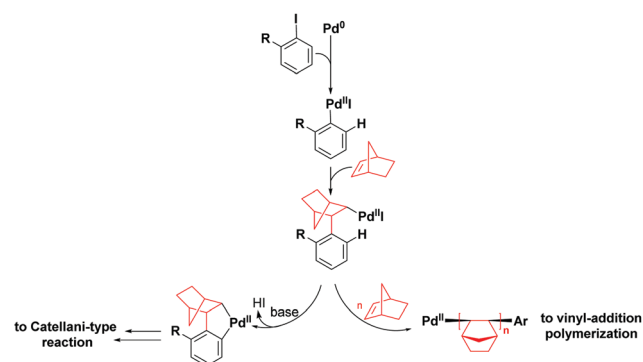
Scheme 2 Possible first stages of Catellani-type reaction[24,28] and addition polymerization of NB (ligands are omitted for clarity).

We have shown here that readily available organic compounds such as aryl iodides and aryl diazonium salts are efficient cocatalysts for activation of Pd(0)- and Pd(2+) complexes for vinyl-addition polymerization. These cocatalysts can potentially replace moisture and/or oxygen sensitive organoaluminium and organoboron cocatalysts in vinyl-addition polymerization of strained cycloalkenes. The metal-free nature of the suggested cocatalysts and the usage of low molar ratios of a cocatalyst/Pd-complex in vinyl-addition polymerization can open new possibilities in the synthesis of polycycloolefins as promising polymeric materials for microelectronic, optical and medicinal applications. The developed systems have catalyzed polymerization of norbornene and its derivatives with hydrocarbonic and polar functional groups in air giving soluble and high-molecular weight polymers. We believe that the proposed approach of using organic compounds as a cocatalyst in vinyl-addition polymerization will provide further insight into the mechanism of vinyl-addition polymerization.

Conflicts of interest

There are no conflicts to declare.

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